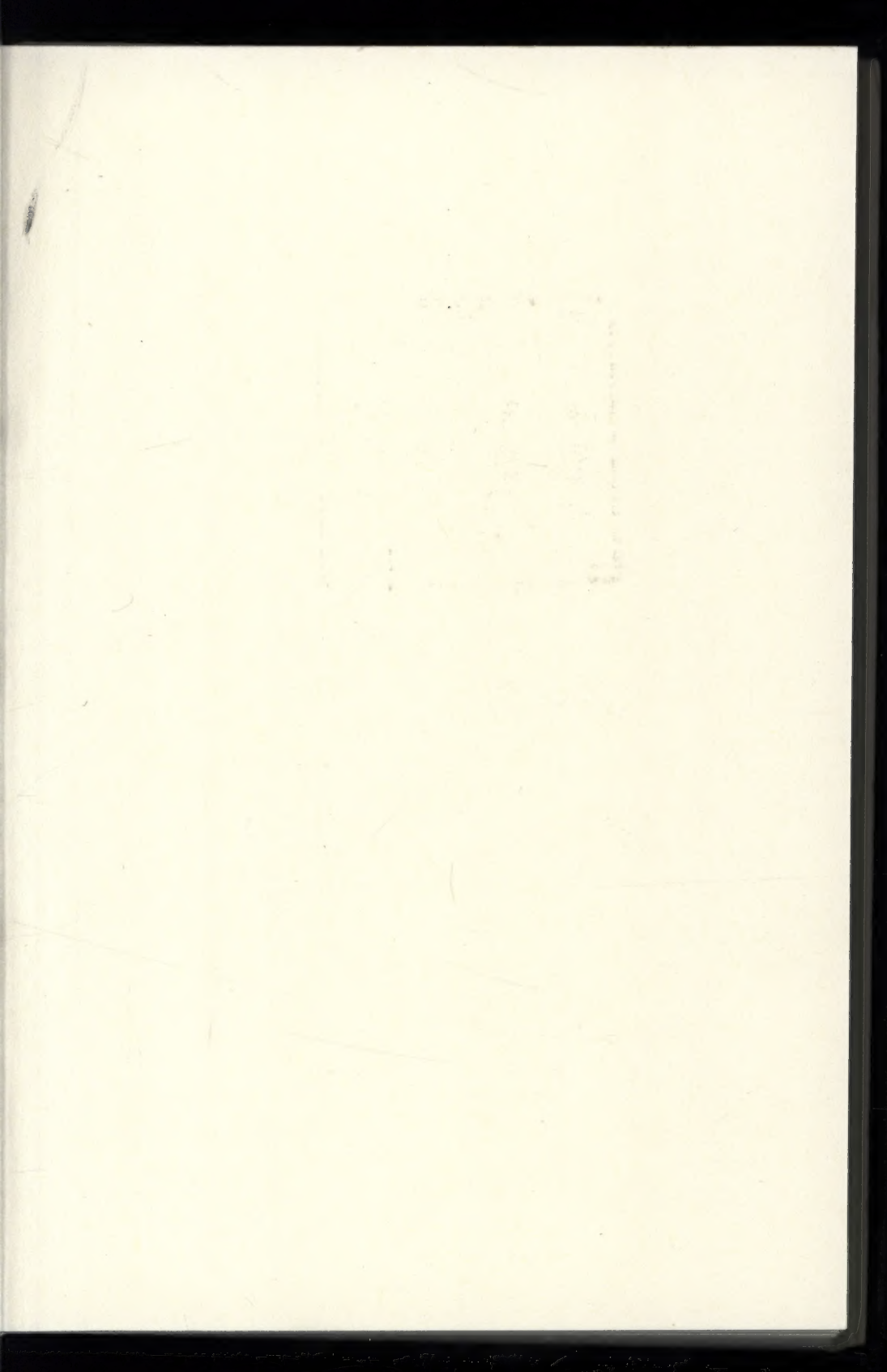


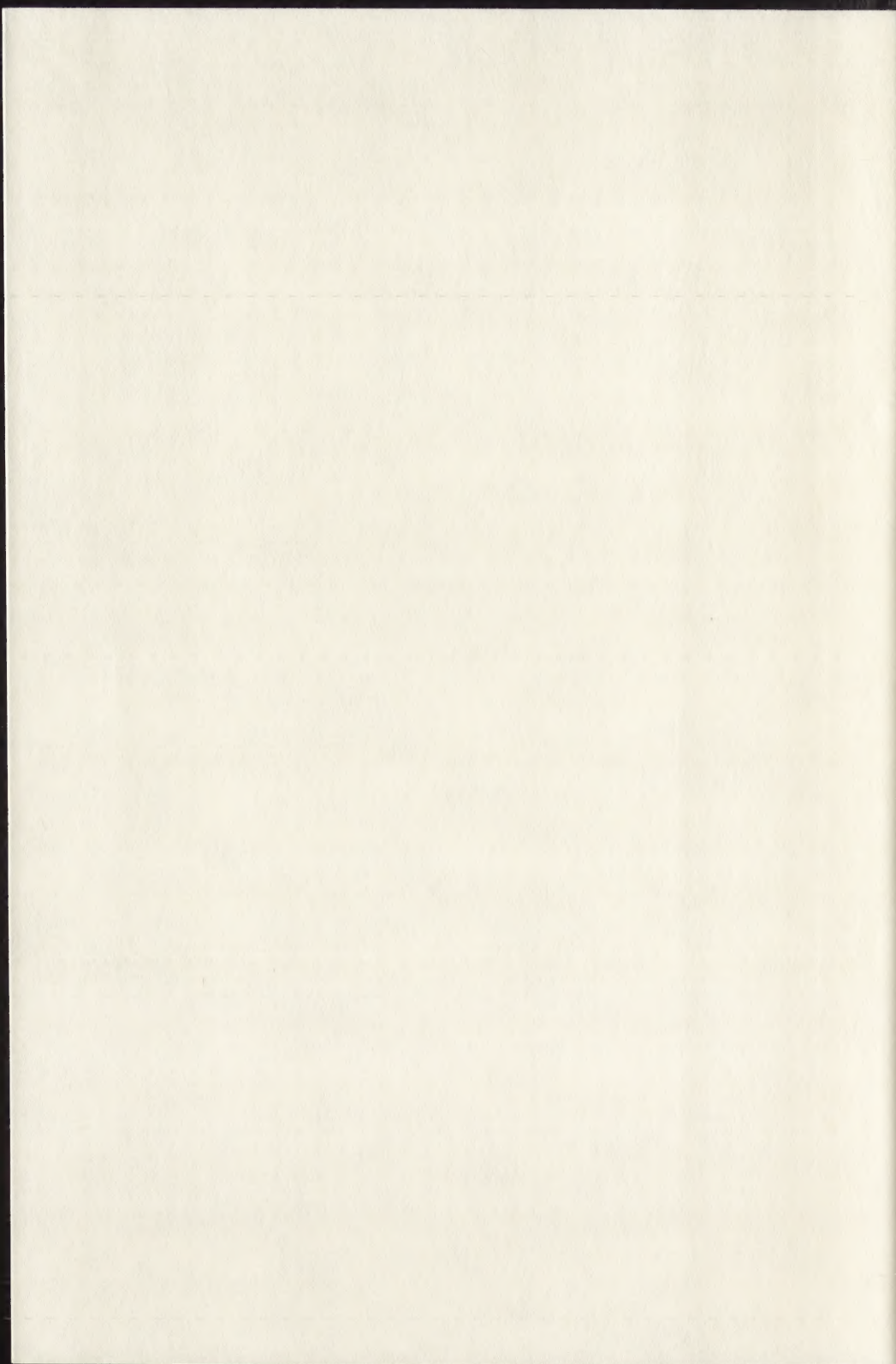
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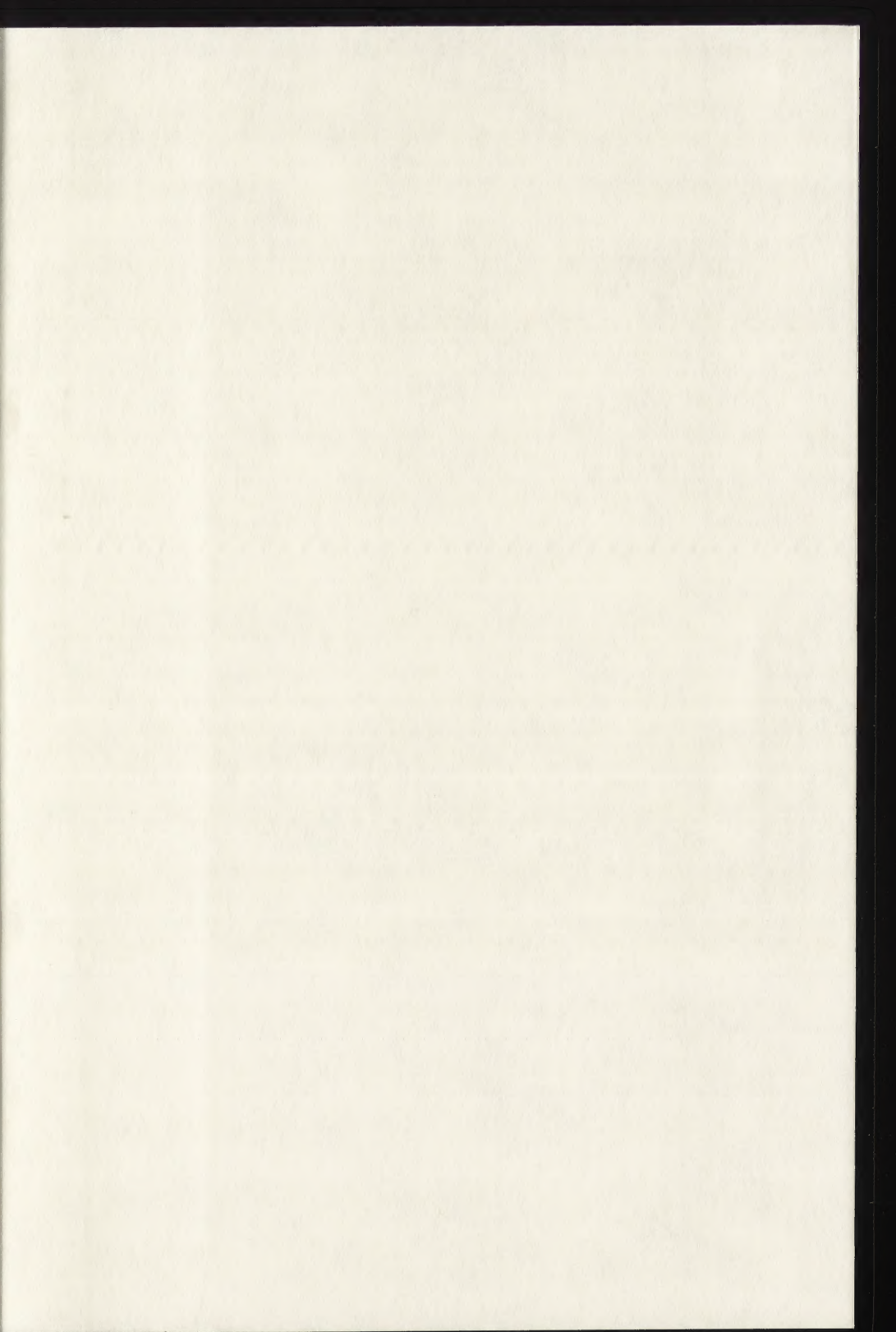


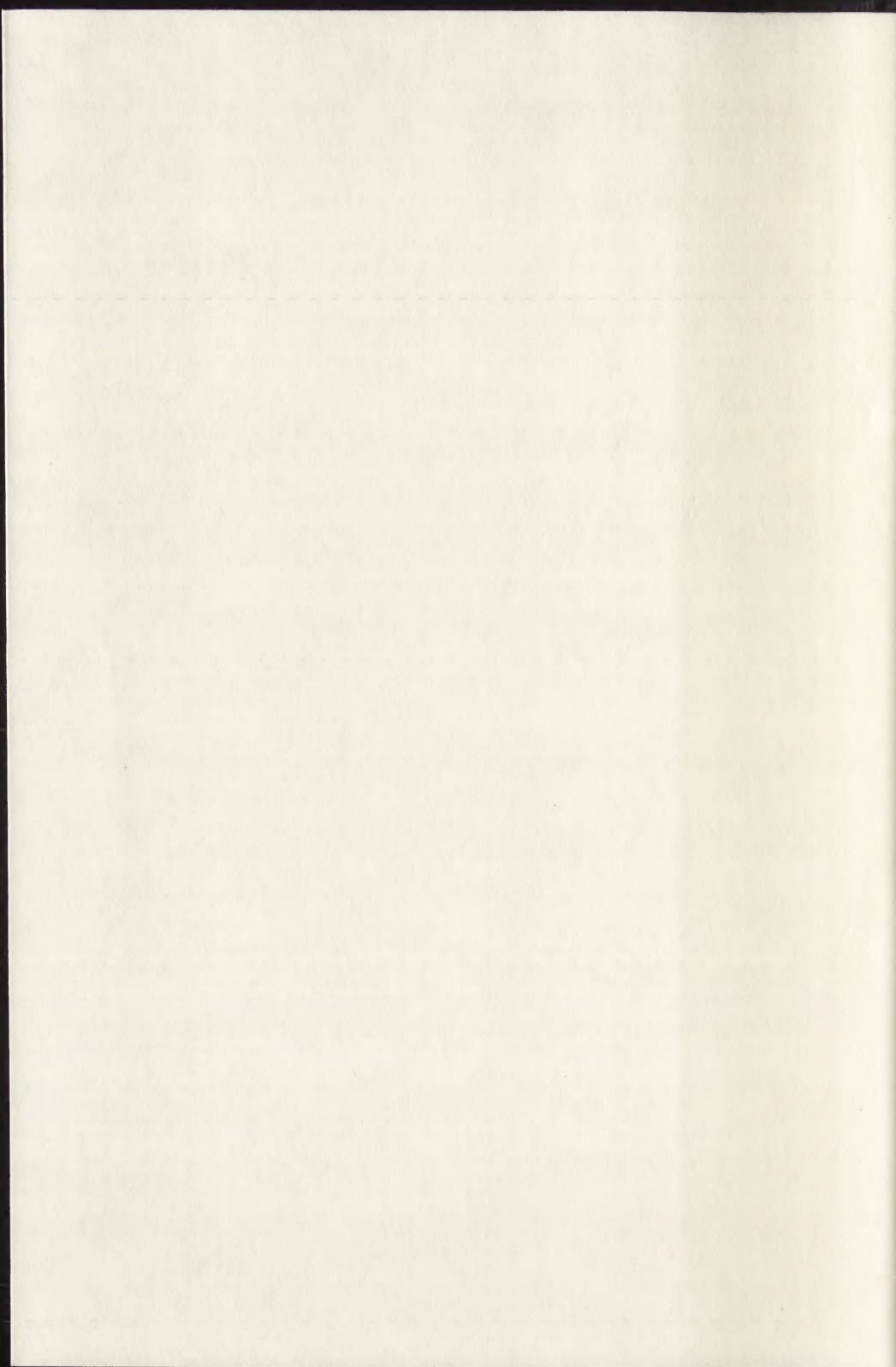
*Why ask for the moon
When we have the stars?*

AS









CONSERVATION OF WATERLOGGED WOOD

Coordinator : R. Munnikendam (Netherlands)
Assistant coordinator:
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Programme 1975-1978

1. Evaluation of PEG process and development of alternative systems for oakwood in a rather sound condition (De Jong, Munnikendam).
2. Development and improvement of chromium-salt preservation (Bouis).
3. Development of the improved freeze-drying technique by pretreatment with PEG 400 (Ambrose).
4. Application of PEG also for partly dried wood (Mihailov).
5. a) Evaluation of the state of preservation of waterlogged wood (anatomic structure, water content, chemical analyses);
b) treatment of objects in the field and in the laboratory using methods developed in the Hermitage (Gerassimova).

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THE CONSERVATION OF SHIPWRECKS

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

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THE CONSERVATION OF SHIPWRECKS

J. de Jong

Summary

In moist or wet conditions wood will degrade under the influence of both microbiological and physico-chemical processes. These processes may cause tremendous changes in both chemical and physical properties of the wood. Decreased strength and increased shrinkage behaviour are well known.

Generally, preserving old waterlogged wood requires a conservation treatment. In the workshop of the Museum for Maritime Archeology at Ketelhaven* large objects are impregnated with polyethylene-glycol 4000. It was found here that European oak having water contents over 185%, when based on dry wood material, could be impregnated successfully with PEG 4000 dissolved in water, and that treatment of less degraded wood required the development of new techniques, of which two are described in this paper.

1. Introduction

In the Lake IJssel Polders many shipwrecks have been discovered in the course of draining and developing the emerged former sea bottom. At present they number over 350, and one may be sure that many more still lay buried in the soil. During the last few years ships have also been discovered at other places in the Netherlands, for example at Zwammerdam (6 roman ships) at Utrecht (2 mediaeval ships), and at Arnhem (1 mediaeval ship). All these wrecks are to be conserved. The principal construction material for ships in this part of Europe was European oak. The permeability of this wood is very low even with respect to water, a condition originating from the presence of tyloses in the wood vessels. Tyloses also strongly obstruct the movement of conserving agents.

When faced with the problem of conserving waterlogged remains of ships constructed of European oak it is essential to know how the degradation of the wood, its shrinkage behaviour, and its chemical composition are related (lit. 1). It is further necessary to obtain information about the results observed elsewhere (lit. 2), and to develop and test new conservation techniques (lit. 3, 4). These three aspects are discussed in the following pages.

* The Museum for Maritime Archeology at Ketelhaven is part of the Scientific Division of the IJsselmeerpolders Development Authority

2. Wood degradation

Wood kept in a moist or wet environment will become waterlogged. In time changes in the physical and chemical properties of the material will adversely affect the suitability of the wood for construction purposes. The principal cause of wood decay is a microbiological breakdown, though physico-chemical processes also contribute to the degradation of the wood (lit. 1, 5, 6).

The rate of decay of a certain piece of wood depends on factors such as wood species, age of the objects, and kind of environment during the time the wood is used and afterwards. In wet and anaerobic situations the breakdown of wood is very slowly. The decay of wood correlates with the increase in the water content of the wet material. When exposed to drying the degraded wood shows a rate of shrinkage well above the shrinkage values given for new wood. The degraded wood structure is unable to stand the contracting capillary forces exerted by the evaporating water during the drying process and often cell-collapse can be observed.

A few illustrative data are given in table 1.

Table 1. The water content and mean shrinkage values of new and old waterlogged European oak heartwood

Origin of the wood	Water content % *	Shrinkage on drying from waterlogged to oven-dry (105° C) (% of the wet dimensions)		
		tangential	radial	longitudinal
New	+ 120	11	5	0,4
Utrecht ships	+ 100	19	8	1
Zwammerdam ships	100-120	21	13	0,5
Bremer Kog	120-145	20	10	-
Utrecht ships	375-415	33	10	10
Zwammerdam ships	275	47	11	13

* the water content is expressed in a percentage of the dry wood material

These data clearly show that increasing degradation of the wood results in a strong increase in shrinkage when the wood is exposed to drying. Under similar conditions even slightly decayed wood may show shrinkage values almost twice as high as new wood.

The degradation of the wood is also reflected in the chemical composition of the material. This is illustrated in table 2.

Table 2. Chemical composition of hard wood (especially European oak) at various stages of decay (mean values)

Origin of the wood	Content of oven-dry wood in percentages				
	water	holocel- lulose	cellu- lose	hemi- cellulose	lignin
Hard woods		60-72	40-50	20-22	28-30
Oak heartwood	+ 120	+ 65	-	-	+ 25
Zwammerdam ships*	98	58	47	11	23
Utrecht ships	131	54	46	8	25
Utrecht ships	455	15	6	9	51
Zwammerdam ships	494	22	6	16	
Swifterbant culture (approx 3500 BC)	-	14	8	6	61

* data for European oak heartwood

This table 2 clearly shows the relation between wood decay and the changes in the chemical composition. It is obvious that celluloses are broken down in favour of lignin. A microbiological degradation of lignin however, has also been taking place as revealed by the high water contents indicating that large parts of the original wood materials have been destroyed.

A very special case of increased wood breakdown can occur in the recently claimed Lake IJssel bottom. Recently emerged land is wet and reclamation of the soil therefore starts with the draining of the land. Removal of the water causes the ground water table to drop, and the toplayer of the soil will gradually become aerated.

As regards a shipwreck the drying of the soil may result in substituting a fast aerobic breakdown of the wood for a slow anaerobic one. The expected lifetime of European oak's untreated heartwood when in contact with an aerated moist soil in a temperate climate is only about 15 years.

This can be illustrated by a chemical analysis of samples of the bottom plankings of a 17th century ship excavated in the Northeasternpolder (Lake IJssel Area). The polder was drained in 1942. The remains of the wreck were discovered in the early fifties, and the wood was described as still possessing a very sound quality. Excavation was delayed until 1976, and it was found that degradation of the parts which had been laying above average ground water level during the time interval between discovery and excavation was severe. A transverse section of the bottom of the wreck was sampled, and the wood analysed for determining its water content and chemical composition. The location of the sampling spots is shown in figure 1, the analytical data are given in table 3.

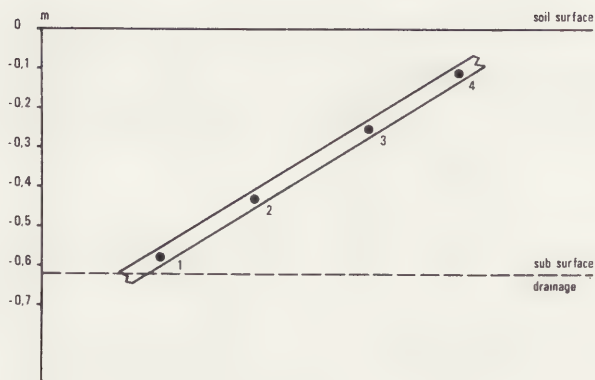


Fig. 1. A schematic representation of a wreck in an aerobic and in a more anaerobic zone of the soil.
1, 2, 3 and 4 indicate the sampling spots

Table 3. The chemical composition* of wood samples corresponding with the sampling spots 1, 2, 3 and 4 of figure 1

Spot	Content in percentages of oven-dry wood				
	water	holocellulose	cellulose	hemicellulose	lignin
1	137	55	41	14	27
2	118	61	48	13	23
3	388	54	42	12	29
4	435	36	26	10	35

* analysis in co-operation with the Dutch Forest Products Research Institute T.N.O., Delft

It is clear that the relatively short period during which the wood lay in a moist aerobic soil was more damaging to the wood than the wet anaerobic soil conditions had been in the previous centuries.

3. Results of conservation with PEG dissolved in water

For processing the ships found at Zwammerdam and Utrecht, and for the more recent finds new, larger conservation facilities have been provided at the workshop of the Museum for Maritime Archeology at Ketelhaven.

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The process used is based on the well-known technique of wood impregnation with PEG 4000 dissolved in water (lit. 1, 2).

This process is only effective with a fair chance of success and within an acceptable length of time (2 years) for European oak of Class I (water content of over 400%), and of Class II (water content from 185% to 400%). Results of these impregnations are now available. A comparison of the impregnation results, as a function of impregnation depth and perpendicular to the longitudinal direction of the wood for Classes I, II and III wood is given in figure 2. Though the treatment processes differ somewhat there is a clear dependency of the results on wood quality.

The following impregnation schemes have been applied to the wood (all objects were of comparable size).

- Class I : the wood is impregnated with PEG 4000 at 60° C. The concentration was raised of from 0 through approx. 90% by weight in a period of 18 months, and then kept at approx. 90% for the next 6 months.
- Class II : the wood is impregnated with PEG 4000 at 30° C. The concentration was raised of from 10% through approx. 50% in a period of 12 months and was then kept at 50% for the next 12 months.
- Class III : the wood is impregnated at 65° C (1, 2). The concentration was raised of from 10% through 60% in a period of 18 months.

From fig. 2 it can clearly be seen that the impregnation results of the Classes I and II wood are considerably better than those of Class I wood.

Regarding the level of impregnation (20-35% PEG based on dry wood) which is given as necessary to ensure stabilization of the wood (lit. 7, 8) the impregnation of Classes I and II wood may be regarded as sufficient.

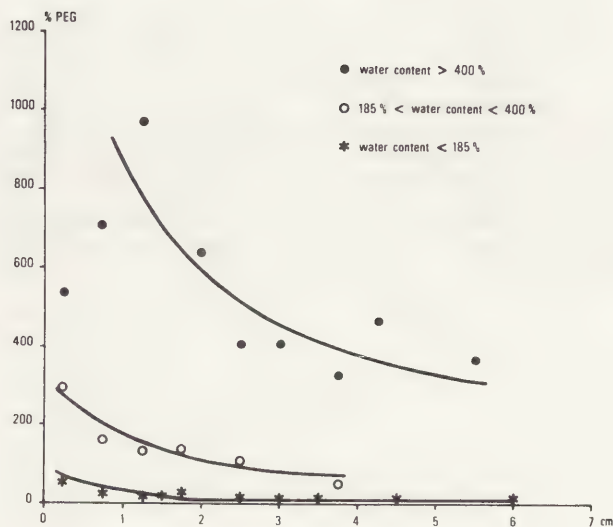


Fig 2. The impregnation results of Classes I, II, and III European oak

4. New techniques

As is shown in fig. 2 impregnation of Class III European oak with PEG 4000 dissolved in water gives unsatisfactory results. Using the warm bath technique shrinkage may occur even during impregnation, and applying the cold bath or spraying techniques the rate of impregnation is not sufficient and in most cases shrinkage will occur after treatment.

For the treatment of large quantities of this Class III wood two techniques were available.

Two techniques developed in our laboratory may give good results. The first technique consists of a dehydration of the wood with tertiary butyl-alcohol (tba) until the azeotropic concentration of the alcohol with water is achieved, an impregnation with PEG 4000 dissolved in the alcohol-water azeotrope at 55° C and a heat treatment. The second technique consists of a simple drying of the wood. This technique can only be applied if the deterioration of the wood is very slight, which limits its value. We have, however, found and excavated shipwrecks consisting either entirely or mainly of wood of in this instance required quality.

The tba-PEG technique

The technique knows three stages. During the first stage the wood is dehydrated until azeotropic composition in tertiary butyl-alcohol, then it is impregnated with PEG-4000 in this alcohol-water mixture and at last after the wood has been taken out of the impregnation tank and after alcohol has been allowed to evaporate, the wood is given a heat treatment to ensure as much diffusion of the PEG-4000 into the cell walls as possible.

During dehydration at room temperature the water is removed from the alcohol by azeotropic distillation. During this stage of the process dark coloured compounds are extracted from the wood. This results in a more natural colour of the dehydrated wood. Besides this the impregnation speed appears to be higher than in the water-PEG process. It was found that the shrinkage occurring during this stage of the process is virtually independent of the dehydration speed.

After dehydration the wood is impregnated with PEG 4000 dissolved in the alcohol-water azeotrope at 55° C. The concentration is raised of from 0 through 50% by volume during 10 weeks (wood samples measuring 20 x 30 x 95 cm) and is then kept constant for another 8 weeks at 55° C. Then the wood is removed from the bath and the alcohol allowed to evaporate for 2 or 3 weeks. At last the wood is given a heat treatment at 60-80° C of from a few days to two weeks.

The result of the treatment is a sound and natural looking wood that only slightly shrunk during the treatment as can be seen from table 4.

Table 4. Mean shrinkage values of Class III European oak, ash and elm at different stages during the tba-PEG 4000 treatment of the wood. Shrinkage as a % of the wet dimensions

Stage of treatment	% shrinkage					
	European oak			ash and elm		
	tangen- tial	radial	longi- tudinal	tangen- tial	radial	longi- tudinal
after dehydration	3.1	1.9	0.4	0.2	1.3	0.1
after impregnation	3.8	2.9	0.7	1.5	1.2	0.0
after evaporation of the alcohol	4.2	3.3	0.8	1.7	2.4	0.5
after heat treat- ment	4.5	3.2	0.8	1.9	3.2	0.6

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As can be seen the observed shrinkages are small. Until now very satisfactory results have been obtained, even with difficult objects, containing little degraded heartwood, highly degraded heartwood and sapwood, and even bark (lit. 4).

The impregnation results as a function of the impregnation depth (perpendicular to the longitudinal direction) are given in fig. 3 for Classes I, II and III European oak heartwood.

The surface concentrations in Classes I and II wood are lower than in the water-PEG process as a result of the lower bath concentration and the heat treatment which allows for a more even PEG distribution. In Class III wood the PEG concentration in the case of the wood is about 12%, which is less than the required levels as indicated in literature. Up to now, however, no problems arose in the treated objects during 2 years after their treatment and storage in both laboratory and (the rather damp) museum of workshop.

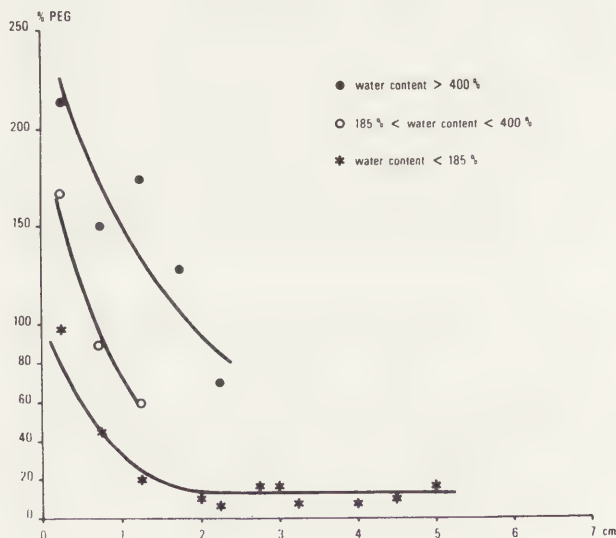


Fig. 3. The impregnation level versus impregnation depth in Class I, II and III European oak heartwood using the tba-PEG 4000 process.

Drying

It will be clear that the tba-PEG 4000 technique is more complicated and expensive than the water-PEG technique. Hence we looked for different, and less expensive possibilities for conservation. It was found that in some instances the wood of wrecks discovered in the soil of the Lake IJssel Polders was of such a good quality that the wreck could be dried at the excavation without the occurrence of large shrinkages, cracking and deformation phenomena. This was observed for a 19th century wreck but also for fragments of considerably older wrecks.

This led to the conclusion that in some instances, when the wood is very little deteriorated, drying of the wood might be a possibility. To investigate this possibility in more detail samples of timber (oak and fir) were taken from a 17th century wreck that is kept under a shower installation in our museum at Ketelhaven. The samples (approx. 200 x 10 x 25 cm and 200 x 4 x 20 cm) were dried under laboratory conditions (20° C, 40-60% r.h.) and the shrinkages measured. It was found that the observed shrinkages were comparable to those occurring in new wood. During the drying of the wood only a very slight surface cracking occurred.

The observed shrinkage data are given in table 5.

Table 5. The mean shrinkage values observed at wood of a very low rate of decay upon drying

wood species	% shrinkage based on dimensions in wet conditions								
	air dry		oven dry				new cur. oak oven dry		
	t	r	l	t	r	l	t	r	l
European oak	9,2	-	0,3	12,1	-	94	10,6	4,8	0,4
fir	4,2	-	0,2	6,3	-	94	7,7	3,9	-

These observations, combined with the collected evidence on the possibilities of drying complete wrecks or large segments of ships, encouraged the start of making preparations for controlled drying of two wrecks in the museum at Ketelhaven. One small wreck (approx. 12 m long) is being dried under controlled conditions, a second and larger one (26 m long) will follow this summer.

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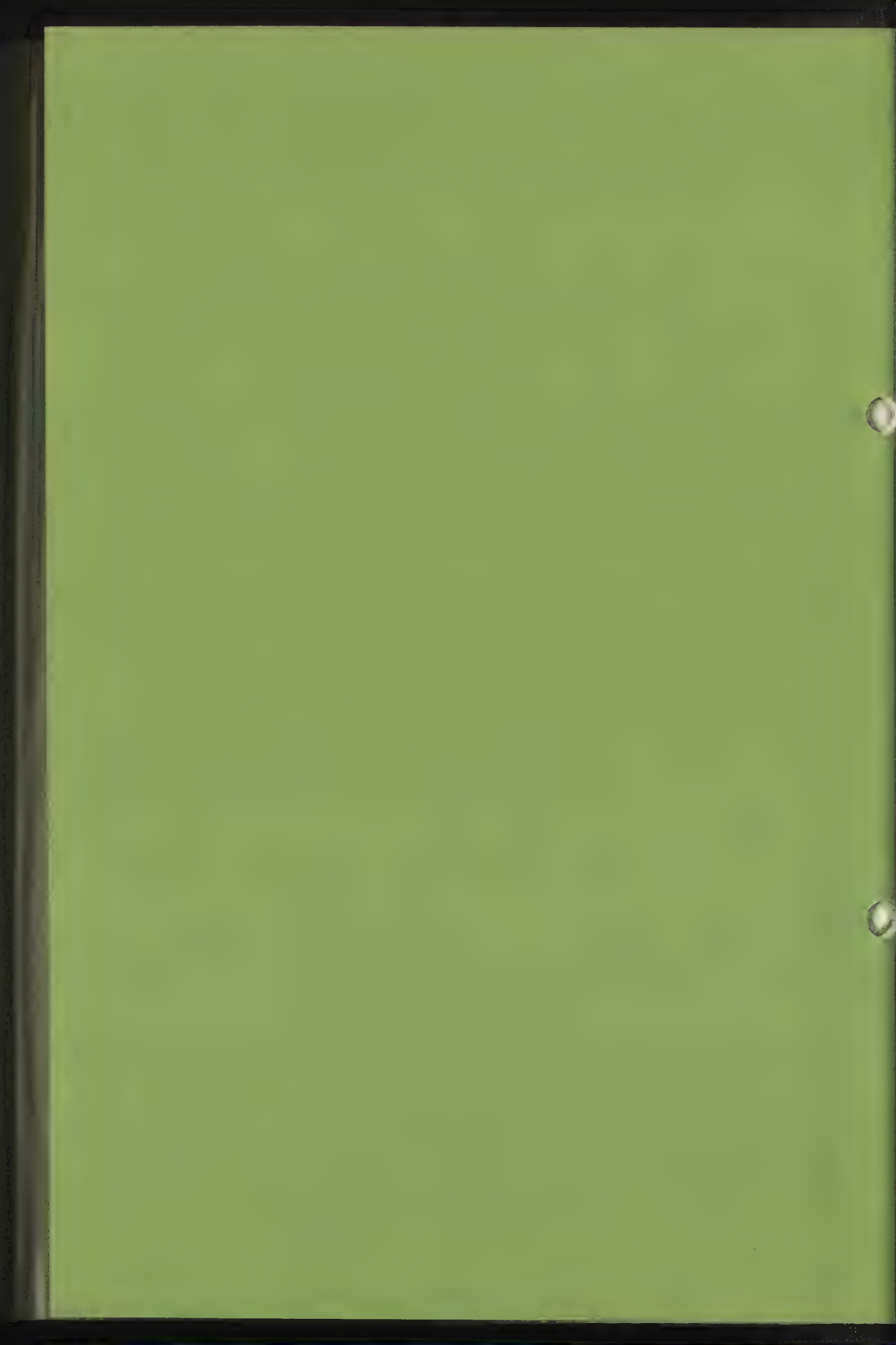
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CONSERVATION OF A THRACIAN ONE-LOG
BOAT

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978



CONSERVATION OF A THRACIAN ONE-LOG BOAT

Anton Mihailov

Our experience till now about the conservation of waterlogged wood gives sufficient evidence to analyse our future activity in this field. We are strongly convinced that in the following 4 - 5 years the method by immersion in a bath with PEG is most perspective. For this reason we continue to use it, but we try to reduce the time of the process.

For that purpose the conservation of the Thracian one-log boat was carried out after analysing the conservation process of an one-log boat from Varna. The time of the process was reduced about 50 per cent, with a very good final result.

In the beginning of 1975 on the sand strip near Bourgas, between the lake of Mandren and the sea and by the former Garda Restaurant the storm had thrown out a one-log made boat (which was determined to be Thracian by the archaeologist Ivan Karayotov). Before it was found, the boat had "travelled" from the lake to the sea and back in the opposite direction to the seashore. By means of microscopic slices Assoc. Prof. Venko Kalinkov specified that the boat had been made of plane mountainous ashtree (*Fraxinus exelsior*). Its maker had rightly accepted this tree type which reaches a height of 35 m. and has a stem diameter of 1.70 m.

The hardness, elasticity and the workability of this type of ashtree are excellent. On the other hand its wood is very resistant to impact loads and it is, therefore, quite suitable for making boats.

The boat has been carved from one tree stem. It has elongated forms of a canoe with a slightly raised bow and a flat bottom. It is 4150 mm long, the middle part width is 600 mm, and its volume is 0.3484 cub.m. The colour of this vessel was dark brown.

The condition of the boat when it was found was quite grave. The stern end was best preserved. On its external part there was an opening becoming narrower in depth, which very likely served for tying the rudder. Its boards have been completely destroyed, mainly by sea worms (*Teredo navalis*), and they were best preserved at the stern side. The upper part of the stern, especially in its right side, was also destroyed by the sea worm. The following major cracks were noticed:

in the bow end, parallel to the starboard with a length of 460 mm, 30 mm wide, in the middle on the portside laterally to the longitudinal axis with a length of 160 mm and 30 mm wide and in the stern side, on the back of the stern, going practically vertically in the upper part 10 mm and 30 mm in the lower part. Due to the long "journey" to the sea and back the bottom in its lower part has been greatly damaged due to friction.

The chemical composition of the wood during the long

time of staying have progressively degraded which was due to the action of microorganisms, temperature, humidity and the chemical reagents of the medium, from aerobic and anaerobic conditions and the pH of the soil. In this process firstly part of the semi-cellulose components decay, followed by the cellulose, and part of the semi-cellulose components and the lignine which is most resistant to chemical effects have remained undecayed. Degradation by about 30 per cent was proved by increasing the maximum humidity and by microscopic observations. This degradation as a result of the stay of the boat for centuries in the water has contributed to the inferior physicommechanical characteristics of the boat, which were mentioned above. In the event of this weakened position of the cellular walls and the existing large cracks ordinary drying would result in large deformations.

The drying up of the ashtree in percentage is not large: 0.2 per cent longitudinally, 5 per cent radially, 8 per cent tangentially and 12.8 per cent in volume. Nevertheless, if incorrect conservation was to be made, the following shrinkage of the size would be produced:

8 mm of the length and about 7 mm in width. This would contribute to a large increase of the old cracks and the appearance of new ones, as well as to certain distortions.

Before treatment the humidity of the surface of the boat was from 32 to 37 per cent, far lower than that in depth. The wetness of the ashtree wood in the point of saturation of the wood fibres is 25 per cent.

At the maximum possible humidity of the sapwood of 43 per cent and of the core of 36 per cent, the bulk density of the ashtree is 0.79 g/cub.cm, the volume of the cellular walls is about 60 per cent, and the pores volume is about 40 per cent. The size of the intercellular spaces is from 10 to 100μ .

The water solutions were introduced in the wood through the tracheas and the tracheides with diameters exceeding 1.2μ . The tracheas have openings of 0.2 - 0.5 mm and are 100 mm long.

According to A. Stam the ratio between the mollecule diffusion coefficient of a given substance in free solution (D_0) and the diffusion coefficient in this substance is freshly cut coniferous wood in a direction longitudinal to the fibres is $D_{lon} = 0.649 D_0$, and in lateral direction $D_{lat} = 0.045 D_0$. The ratio between D_{lon} and D_{lat} is 14.4. If penetration in the ashtree is the same (and it is not smaller) then the selected regime in time duration shall be longer than the theoretical time of seeping into the boat.

The mode in which the ashtree boat was conserved is a product of that in which another one-log boat made of *Quercus Frainetto* Ten was conserved a few years ago, exhibited in the Varna District Archaeological Museum. The difference of the modes is as follows: (a) The Varna boat: time of bath conservation 475 days; concentration of the initial solutions of PEG (polyethyleneglycol) was 7, 8, 9 & 10 per cent; maximum solution concentration 90 per cent; minimum solution temperature 15°C ; maximum

70°C; maximum absolute humidity of the destroyed wood 140 per cent and minimum at the end of the conservation process 16 per cent. (b) Bourgaz Boat: time of staying in the bath - soaking in 1 per cent PEG solution to reach the maximum possible moisture 23 days and conservation by the relevant mode of 239 days, or a total of 262 days; concentration of the initial solutions 5,6,7,8,9 and 10%; maximum solution concentration 95%; minimum solution temperature 20°C, maximum 66°C; maximum absolute humidity of the destroyed wood reached after soaking 73%, and minimum at the end of the conservation period 15%.

These differences were dictated from the following considerations: the reduction of the initial solution concentration from 7 to 5% was made because of the lower maximum humidity of the boat wood; the increase of the maximum solution concentration from 90 to 95% was intended so that the boat humidity should not exceed 15%; the maximum temperature was reduced from 70° to 66°C because the boat had several initial cracks, some of which reached up to 30 mm in width, and at higher temperatures they would further extend; the length of the conservation process time was decreased by 50% because of the established reserves in the boat conservation regime of the Varna boat and because of the relatively lower initial absolute humidity of the boat wood, of which 61 days were removed.

The conservation process ended when such characteristics were obtained securing end boat humidity of 15% which correspond to the mean annual equation

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humidity in Bourgas. The polyethyleneglycol (PEG) absorbed by the boat, established by measuring its residue in the bath was 237 kg. By computation, the amount of the absorbed PEG should be the following: at maximum reached absolute humidity of the destroyed wood 73% and maximum humidity of the freshly cut ashtree wood 47.4%, we have an increase of the porosity from 40 to 70.7%. In such case the volume of the pores is 0.246 cub.m. At the average volume weight of PEG 1500 and PEG 4000 of about 1.170 and 85% filling of the pores, the amount of PEG which should be absorbed by the boat is 245 kg. This amount with fairly great accuracy corresponds to the actually absorbed amount of PEG.

Only PEG 1500 (with lower viscosity than PEG 4000) was used at the beginning in order to secure its absorption in the central part of the boat.

As between the ashwood density and the average specific gravity of the two PEGs there is a difference of about 30%, the weight of the boat was also increased to a certain extent. But in the process of conservation at the lower solution concentrations the boat would have emerged, and for this reason it had to be pressed down.

In order that no deformations in reducing the absolute humidity of the wood from 25 to 15% are obtained, the regime was greatly elongated and its duration for this difference of 10% was 129 days, or 50% of the whole duration of the process. Here are also included the last 31 days when the boat stayed in the bath at 85% concentration and temperature of 64°C.

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The conservation of wood which had remained centuries in ground and other waters is in principle made by methods which would preserve the volume to a maximum, such as the PEG methods. As the surface moisture of the wood was higher than that of the point of wood fibre saturation, a regime was selected with preliminary complete soaking with water before starting the conservation. For 100 days the boat was sprayed and poured with water several times a day and after each wetting it was covered by polyethylene foil. Then for 40 days it was applied with 1% PEG 4000 solution three or four times a day in water and then 25 days in 2% and 3% solution.

After the bath and the raising mechanism were mounted, the boat was placed on wooden supports (blocks) and was pressed by stone slates. Then 2 tons of 1% PEG 1500 solution in water was poured. 0.2% sodium pentachlorophenate was added for anti-septic and the boat remained in this solution 24 days so that it can be completely soaked with water.

Further on the conservation process was carried out as follows (Table 1): from 5% to 10% solution the increase was made every 1% in order that no intensive diffusion is obtained, as a result of which PEG would accumulate on the surface layers. This, on the other hand, would make more difficult the further penetration of the artificial wax; from 10% to 95% the solution concentration was increased every 5%; from 5% to 30% for solution was used only PEG 1500 (for better penetration) by adding 0.5% SPCP; from 30% to 40% PEG 4000 was added, which in relation with PEG 1500 was 1:4 weight parts -

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- the gradual increase of PEG 4000 was done in order to increase the hardness of the stabilized mass; from 40% to 55% to the solution was added 0.5% glycerine; from 60% to 75% - 1%; from 80% to 95% - 1.5%, and from 90% to 80% (by lowering the concentration) - 2%. The glycerine was added as plastifier and in order to prevent the accumulation of PEG on the wood surface by forming a molecular layer(film) around the macromolecules. This, on its part, increased the distance between the individual macromolecules, making them mobile, thus facilitating their penetration to a greater depth. From 45% to 55% the ratio between PEG 4000 and PEG 1500 was raised to 2:4, and at 75% reached 3:4, at 80% was raised to 4:4, which ratio remained to the end of the process. The temperature was raised from 20° to 64°C and heating was made by electric heaters. The solution was periodically stirred by blowing with vacuum cleaner in order to avoid any PEG sedimentation on the bath bottom and the top surface of the boat. During the period of conservation the boat was raised up on several occasions to control the course of the conservation regime.

In order to prevent any transgression of the SPCP which is soluble in water into a pentachlorophenol which is not soluble in water, the pH acidity of the solution was maintained within the range from 7.5 to 10.

After reaching the maximum solution concentration (95%), the concentration was reduced to 85% in order to equalize the PEG quantities along the whole section of the boat. After the conservation

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process ended, slow cooling of the solution to 50°C was made. At that temperature began the removal of the boat at stages of 5 cm. After each raising the still hot part was cleaned by pads soaked in ethyl alcohol. The finally raised boat was "launched" on wooden polished surfaced placed on top the bath. On this "platform" the boat was cleaned -its side and bottom surfaces. The final cleaning was made by heating the whole top and side surface by ^{lamp}Inf.R. (by means of which the drying of the surface treated with methylated spirits was made).

The protective treatment was made by two-fold application of 3 weight parts of Cosmoloid (microcrystalline wax) 2 weight parts, Paraloid B 72 and 95 weight parts toluene.

After this treatment the boat was exhibited in one of the halls of the Bourgas District People's Museum.

CONCLUSIONS: The corrected regime of conservation of one-log boat made of ashtree wood, in comparison with that for conservatinn of one-log boat made of oak proved to be more adequate because it reduced the conservation process by about 50% with the same final results.

After the two regimes and the dynamics of the conservation processes is compared, the corrected (reduced) regime can be recommended in similar cases for relatively large works made of wood which had stayed long in water.

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Table 1
REGIME FOR THE CONSERVATION OF THE BOAT

Solution concent- ration %	Specific weight of sol. g/cub.cm	Tempe- rature C°	Absol. humid. of wood %	Time of pro- cess days	Notes
1	2	3	4	5	6
1	1.002	20	37-43	23	Increasing humidity to 73%
5	1.008	20	73	5	Zone above
6	1.010	20	71	3	the point of
7	1.012	20	69	2	sturation of
8	1.014	20	67	2	wood fibres-
9	1.016	20	65	2	accelerated
10	1.018	25	63	7	regime
15	1.023	30	57	7	
20	1.031	35	52	8	
25	1.037	38	47	8	
30	1.042	40	43	8	
35	1.048	42	40	8	
40	1.054	45	37	9	
45	1.062	48	34	9	
50	1.071	50	31	9	
55	1.076	52	29	9	
60	1.081	54	27	11	
65	1.086	56	25	11	
70	1.091	58	23	12	129 days de-
75	1.100	60	21	13	layed regi-
80	1.105	62	19	14	me in the zo-
85	1.110	64	17	16	ne under
90	1.115	66	15	16	point of sa-
95	1.120	66	14	7	turation of
90	1.115	66	15	12	wood fibres
85	1.110	64	15	31	(25%) of

Total number of days: 262 of which
23 for soaking the boat.

NOTE: The specific weight of the
solutions to 70% was measured at
20°C, and above that at 40°C.

ashtree. Fi-
nally a 31-
day treat-
ment is ma-
de at 85%
concentra-
tion and te-
mperature of
64°C in or-
der to equa-
lize moistu-
re of wood
along whole
cross sect.

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TESTING NEW TRANSPARENT SILICONORGANIC
AND SOME ORGANIC POLYMERS FOR CONSERVATION
OF ARCHAEOLOGICAL WOOD

Natela Yashvili

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

TESTING NEW TRANSPARENT SILICONORGANIC AND SOME ORGANIC
POLYMERS FOR CONSERVATION OF ARCHAEOLOGICAL WOOD

Natela Yashvili

Man began to utilize wood from time immemorial. Wood was used for making weapons, utensils, adornments, musical instruments, also for building boats, ships, bridges, swellings, means of conveyance etc. These wooden structures and objects of the everyday life excavated by the archaeologists are of a great historical value and great importance is attached to their conservation.

In the soil wood undergoes changes arising from the most diverse reasons. Thus, for example, oxidation and hydrolysis of the constituent organic substances (hydrocarbons, tannins, oils etc.) of wood occur under the action of water, air oxygen, the acid and alkaline reaction of the soil and microorganisms.

It is believed that the intensive destruction of wood of archaeological findings begins at the moment when the object comes into contact with the surface layer of the soil. From that moment onwards wood is most intensively subjected to the influence of atmospheric precipitation, temperature variation and to the action of wood-fretting microorganisms.

With lapse of time the object becomes buried in the cultural layer. In the course of 8-10 centuries the object may get buried to a depth of several metres. High soil humidity and the absence of ground water motion exert a conserving action on wood and thereby decrease the rate of its degradation. Nevertheless, the wood destruction process continues. Since

wood is water-logged, solution and hydrolysis of polysaccharides take place. Thus, when buried in the soil, wood, being the product of the organic nature, is changed to a considerable extent. The dark colouring, decrease in hardness and strength, high water absorption and shrinkage arise from the fact that the chemical composition and microstructure of such wood undergo essential changes. The extent of wood destruction depends on many factors, in particular on a wood species and on how long and in what conditions wood remained in the humid soil.

It is not infrequent that archaeological wood that had been buried in the peat-bog for a long time preserves its shape and dimension just owing to the fact that the weakened and halfdestroyed cells are saturated with water. After water evaporates, the cell walls shrink and the object gets deformed and develops cracks. The reason for this is that in the object buried in the soil a slow destruction of the cellulose components of the cell walls occurs and as a result the mechanical strength of wood decreases.

In drying wood preserves its shape and dimension till there remains 25-30 per cent of water. If drying continues beyond this point, corresponding to the saturation point of the adsorbed water, essential changes occur in the cell walls and cracks are developed. Upon evaporation of water the surface tension of the wood substance exerts a certain action on the weak cells which cause destruction of wood. The dry material content in old wood is less than half of the content in fresh wood because in aging the cells lose part of their cellulose. As a rule, in drying greater changes are observed in old wood than in fresh wood.

Prior to starting conservation wood must be treated with antiseptics.

In case archaeological wood is darkened with time, it may be bleached with a 5 per cent solution of hydrogen peroxide, such a treatment permitting to restore its natural colour.

For stabilization of archaeological wood we tested transparent (polymethylphenylsiloxane, polymethylsiloxane, polyphenylsiloxane, polysiloxane, polyamino-hydrosiloxane, polycyclosiloxane etc.) and organic (TH-30 striol and PH-71 nonstriol) polymers.

We treated with polysiloxane polymers the exhibits of archaeological wood (a vat, a cup, a three-legged vase, a dish, a comb, wooden supports from the ancient adit) excavated in Bedeni and dating back to the 23 - 21 centuries B.C.

Prior to the treatment of the exhibits anatomic and microchemical analyses of wood of the supports from the ancient adit were carried out. The results of the analyses enabled us to identify ten specimens as the beech (*Fagus*), two specimens as the yew or the red wood (*Taxus baccata* L.) and one specimen as the elm (*Ulmus* L.).

For conservation of this wood a method was developed, consisting in deep impregnation of wood with the transparent emulsion of the polysiloxane resin; the latter passes subsequently into a solid state by means of thermal treatment.

The humidity and density of wood were determined at several points along the radius and length of the beams. The wood from the ancient adit proved to be nonuniform. The average density value of wood in the absolutely dry state was 0.26 g per cu. cm, while the humidity value ranged from 40 to 21 per cent.

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To effect conservation it was necessary to replace water contained in wood by the synthetic resin at comparatively low temperature.

The aqueous emulsion of the polysiloxane resin was applied by means of a brush. The beams were coated with the emulsion three times a day. Next, the beams were impregnated with the emulsion under pressure in the apparatus specially designed for deep impregnation.

Depending on dimension of the exhibits, thermal treatment was conducted either in the thermostat or by means of infrared lamps by slowly raising temperature from 40° to 100°C in order to ensure smooth drying of wood.

After thermal treatment had been completed, the state of the wooden supports was radically changed. All the beams had acquired a firm, 4 - 5 mm thick, coating reinforced with the siliconorganic resin, underneath of which was though less impregnated but still well reinforced internal part of wood.

Small-sized exhibits (a three-legged vase, a jug, a vat, a cup, a dish, a comb and various vessels) dating back to the 23 - 21 centuries B.C. were treated with the α, ω -di(methacrylatemethyl)dimethylsiloxane oligomers with the number of siloxane links being $n = 12$.

Preliminarily, the wooden objects which were darkened with time were bleached with a 5 per cent solution of hydrogen peroxide. After bleaching the surface of some exhibits displayed ornaments. Then, using V.V.Krystensen's method, wood was dried in several ethyl alcohol baths with a subsequent dipping in ether baths. After that the transparent liquid oligo-

with a catalyzer was introduced into wood and polymerization was carried out in the pores of the wooden object at temperature of 55 - 60°.

The amount of the polymer retained in the specimens was determined by weighing. As one should have expected, the polymer content in the specimens with a higher dry material content was less than in soft wood.

Dimethylsiloxane oligomers with methacryl groups at the ends are used as liquids with subsequent polymerization in the pores of wood which is being reinforced. They possess a number of advantages in comparison with the methods commonly used. The surface treated with such oligomers remains quite natural. The colour of wood is not changed and the surface does not glitter. The specimen shrinks rather insignificantly. Cracks are not developed. The treatment procedure is very simple and consumes little time.

To verify the conserving properties of the aforementioned siliconorganic compounds they were used for impregnating the cubes made of archaeological wood dating back to the 17th century B.C. To find out how the treated wood withstands atmospheric influences the specimens were alternatively subjected to sharp variations of humidity and temperature. Maximum temperature for thermal aging was taken 50°C. Six months of such artificial aging yielded satisfactory results.

Thus, good results are obtained when conservation of historical exhibits of the organic origin is effected by means of the transparent siliconorganic polymers of different structure; depending on a species and a degree of preservation of the exhibit it is possible to use liquid oligomers, solutions or emulsions of siliconorganic polymers of different structure.

REFERENCE MATERIALS

Coordinator : J. Winter (U.S.A.)
Assistant coordinator:
Members : N.S. Baer (U.S.A.)
E. Bosshard (Switzerland)
R.L. Feller (U.S.A.)
F.G. Poole (U.S.A.)
S.G. Rees-Jones (U.K.)
R.E. Stone (U.S.A.)
R. van Schoute (Belgium)
M.L. White (U.S.A.)

Programme 1975-1978

1. Compilation of a guide to commercially available reference materials (Winter).
2. Methods and standards for the replication of X-radiographs, and the encouragement of centers for doing this (Baer, White).
3. Standardization of radiographic methods. Survey and development of standard penetrometers for use in the museum field (Stone, Bosshard).
4. Survey and inventory of existing collections of radiographs and related materials. Information exchange on this subject (Rees-Jones, Van Schoute).
5. The development of reference collections of pigments used in the museum field. Information exchange on this subject (Feller).
6. The development of reference collections of materials used in paper and archival conservation, especially from the point of view of retaining maximum information about materials used in treatment, and to follow their later behaviour (Baer, Poole).

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REFERENCE MATERIALS IN THE CENTRAL
RESEARCH LABORATORY

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

REFERENCE MATERIALS IN THE CENTRAL RESEARCH LABORATORY

J.A. MoskABSTRACT

Some considerations are given on the division in groups of the reference materials in the collection of the Central Research Laboratory. A distinction is made between specimen or example materials and standard materials, depending on the quality of the information available. Furthermore the name 'standard objects' is suggested for more complex materials which may be used in studies regarding the ageing of materials. The criteria to which a material must answer before one can call it an example material or a standard material are discussed briefly, together with the way the materials can be used.

A survey is given of the collection of the Central Research Laboratory. Some manufacturers or distributors of parts of the collection are mentioned.

INTRODUCTION

The Central Research Laboratory for Objects of Art and Science in Amsterdam, Netherlands, owns over a thousand labeled vials and cardboard boxes, containing materials that are related to art materials, the dying trade or geological materials. The available amounts range from less than 1 gram to several hundreds of grams. Until now these samples were regarded as "The collection of reference materials" of the Central Research Laboratory. In the light of the considerations with respect to the subject of Reference Materials, as worked out by John Winter in his Worknotes of October 1976, this appreciation of the collection should be reconsidered and refined.

DIFFERENTIATION

First I have come to the opinion that many of the samples meet the 6 criteria formulated in Winters Worknotes (p.2) inadequately. This circumstance, however, does not make this part of the collection

uninteresting or useless to workers in the field. Only, these samples should not be called Reference Materials in the sense of completely analysed, fully recorded, materials. They have a lower level, less quality of information; the only thing many of them have is their name. Their names should give the researcher insight in their composition and their function. These materials are examples of forms which may be encountered in the examination of works of art or scientific objects. As such the example materials can meet several needs of the researcher:

- they are an example of how the material may look like
- they provide positive tests as compared with blanks
- they show, better observable than with a minute sample, the properties of the material (they can thus be used for demonstrative purposes in education).

Criteria for the status of example material are:

1. that the material must be present in a form in which the product occurs in the course of the process in which it is incorporated in the art-object.
2. that the name is known and that it is applicable to one material only.
3. that the stage of the process meant under 1. is indicated.

The name "standard material" should be applicable to well defined, well recorded and accurately analysed samples.

Criteria standard materials should answer to, are:

- an accurate analysis of the composition is available, so that the material can be used to standardize quantitative analytical measurements.
- the origin and the method of manufacturing or preparation is well-known, so that, e.g., in the case of vegetable material, it can be established whether the standard material or a well-defined derivative is present in a sample of an art object (e.g. resin, gum, medium, dyestuff).

Typical standard materials are:

- analytical grade reagents
- analysed alloys
- pigments or dyestuffs of which the origin, method of manufacturing, composition, particle characteristics etc. are well-defined or analysed accurately.
- wood specimens together with the three characteristic thin sections of the wood species, if provided with the systematical Latin name and place of origin.
- fibre preparations of vegetable or animal origin, if provided properly with a name; also chemical fibres of well-known composition and method of manufacturing.

I would not say that analysis of trace elements is a requisite in this category. If a trace pattern is to be investigated, the standard material(s) can be analysed along with the sample(s).

It may be noted that a reference material with the status of an example can be promoted to the status of standard by the acquisition of

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the proper analytical and circumstantial information. (Cf. the "up-grading" of collections mentioned by John Winter in his Worknotes of October 1976, p. 4).

STANDARD OBJECTS

Materials that are to be used in the study of changes of art-objects undergone with time of exposure to various influences are likely to be of a more complex character than the materials discussed above. I think of paints, dyed textiles, experimentally made paintings, ceramics or enamels etc.. In connection with this type of experiments I suggest the name of "standard objects" instead of reference materials. (Cf. The Reference Cigar, mentioned in the memorandum to members of the Working Group of John Winter, April 1976. I think this cigar is meant to be a standard object as to certain properties.).

DIFFERENT KINDS OF MATERIALS

It is preferable that the criteria which can be formulated for example and standard materials are not used as absolute requisites. With this concept in mind it will be possible to place any sample in the most appropriate class. A short discussion of the situation with pigments will illustrate this point.

A pigment in a paint sample is characterized by a number of properties:

- chemical composition
- microscopical appearance, crystal-optical properties
- grain-size distribution
- trace pattern
- colour

The appropriate reference material, even if it is a standard material, will have its own set of properties, which will, to a certain degree, be different from that of the pigment in the sample. One can say that the "standard material" falls back to the status of "example material" with respect to the identification. Especially in samples of natural origin there is so great a number of variables in the properties to be observed or measured, that it is very unlikely that the sample is exactly identical - in every aspect - to the reference material.

LISTS OF NAMES

The files on the collection of the Central Research Laboratory contain the names of over a thousand samples and materials, subdivided in groups according to the kind of material or the source or the distributor of the material. Each sample carries a UDC number (Universal Decimal Classification), an order number and a localization number. The list fills 41 closely typed A4 pages, it will therefore not be included in this report. It will be handed to the members of the Working Group and can be ordered by those who are interested. It contains the names of 292 pigment samples, most of which are a gift of the Doerner Institut in Munich. There are 200 natural resins,

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gums and glues, 509 geological and mineralogical specimens and 278 materials of which most are vegetable. Most of these 278 materials are for the dying trade. The Laboratory has also the possibility to use standard alloys, owned by the University of Amsterdam, bought from several manufacturers. A few examples are given in table I. The distributors for some materials are given in table II.

NOMENCLATURE

The names and descriptions in the files are in several languages: Latin, Dutch, German, English. It may already be concluded from this, that work has to be done to make the information accessible to anyone interested in the subject.

I suggest that a three or four language dictionary is compiled (English, French, German and Latin if applicable), arranged in alphabetical order and divided in groups of materials, the way it was done in the encyclopedia by R.J. Gettens and G.L. Stout "Painting Materials" (Dover Publications, Inc., New York, 1966).

Alloys may be arranged according to the element names of the main components. To prevent equivocal nomenclature I suggest that the members of the Working Group send their lists around and complete each other's nomenclature. Afterwards, the lists can be subdivided and put in alphabetical or any other systematical order.

ACKNOWLEDGEMENT

As a member of the Working Group on Reference Materials I feel the need of expressing gratitude to those who - in past and present - paid attention to the gathering of materials and to the documentation and preserving of the collections, within the Central Research Laboratory and outside, especially to the staff of the Doerner Institut who donated hundreds of samples of their collection to the Central Research Laboratory as early as 1966, which formed the start and the nucleus of the collection.

TABLE I

British Chemical Standards, issued by the Bureau of Analysed Samples Ltd, Newham Hall, Middlesbrough, England.

High speed steels

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No.	Fe %	W %	Cr %	V %	Mo %	Co %	C %	Si %	S %	P %	Mn %
SS481	rest	14,2	3,56	0,52	0,22	0,21	0,69	0,14	0,027	0,021	0,29
SS482	,,	18,1	4,09	0,98	0,27	0,24	0,70	0,13	0,025	0,021	0,28
SS483	,,	10,8	3,21	0,54	0,17	1,94	0,67	0,11	0,025	0,019	0,29
SS484	,,	22,4	5,17	0,94	1,07	10,2	0,85	0,20	0,024	0,030	0,21
SS485	,,	18,2	4,15	1,05	0,67	5,06	0,89	0,42	0,043	0,046	0,50
SS485	,,	6,48	4,53	1,91	5,23	0,13	0,74	0,14	0,029	0,021	0,12

Si Aluminium Alloys

No.	Al %	Si %	Cu %	Mg %	Fe %	Mn %	Ni %	Zn %	Pb %	Sn %	Ti %
SS501	rest	8,8	0,20	0,51	0,70	0,11	0,24	0,01	0,22	0,11	0,19
SS502	,,	10,0	0,44	0,67	0,20	0,61	0,07	0,21	0,17	0,21	0,10
SS503	,,	11,1	0,10	0,31	0,11	0,70	0,30	0,15	0,14	0,07	0,13
SS504	,,	12,0	0,27	0,21	0,50	0,31	0,02	0,06	0,07	0,03	0,17
SS505	,,	12,8	0,05	0,05	0,30	0,52	0,20	0,24	0,09	0,17	0,03
SS506	,,	13,9	0,02	0,12	0,40	0,21	0,13	0,30	0,02	0,13	0,07

Note.

The percentages represent average values of in most cases ca. 10 independent measurements. All these measurements are registered in the Certificate of Analyses, so that it is possible to assess its accuracy. Two typical examples are in SS 481 W = (14,23 + 0,04)% (standard deviation = 0,3 %) and S = (0,027 + 0,002)% (s.d. = 8%).

TABLE II

Geological and Mineralogical Samples:

Dr. F. Krantz, Bonn am Rhein, German Federal Republic (Baugesteinen für Aussengebrauch, mit Dünnschliffen; Building Stones for outdoor use, with thin sections) (Mineralien, systematisch geordnet nach Brauns-Chudoba "Spezielle Mineralogie"; Minerals, systematically put in order, after Brauns-Chudoba "Spezielle Mineralogie", Special Mineralogy).

Natural Dyestuffs:

Wide World of Herbs Ltd., successors to Dominion Herb Distributors
11 St. Catherine Street East
Montreal, Canada, H2X 1K3

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REPORTS ON REFERENCE COLLECTIONS

John Winter

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

REPORTS ON REFERENCE COLLECTIONS

John WinterAbstract

A series of "Reports on Reference Collections" is proposed. Each report would summarize the holdings in reference materials of a museum laboratory. Suggested guidelines for the scope of such reports, the definition of what may be included, and the information that should be given are discussed briefly.

Introduction

Many museum laboratories have collections of what may be loosely termed "reference materials," (1). As a method of documenting these collections, and improving collaboration among potential users, the co-ordinator is proposing a series of "Reports on Reference Collections." Each report would be a concise but detailed statement of the holdings of relevant materials in a particular laboratory. In October 1976, a set of "worknotes" on this subject was circulated to members of the working group concerned with this project (J.A. Mosk and R.L. Feller). The present paper is condensed from those worknotes.

Some discussion is first needed on two broad questions: a definition of what should be covered and the information about the material that should be expected in a report.

Definition

1. For these Reports, I suggest we confine ourselves to material samples or specimens, rather than documentary matter. This would rule out photographs (including radiographs), chart recordings and so on.

Radiographs and infrared photographs have been covered separately in the past (2). Some kinds of photographic records may fall more naturally into the Documentation Working Group. Anyway, most laboratories probably organize their "material" reference materials separately from documentary matter.

2. By "reference materials" I suggest that we mean things that form a reference point for present or future work, and not samples whose primary purpose is as part of the record of a past investigation. The question here is how far samples taken from objects (including cross-sections and other microscopic preparations) are "reference materials", and how far they are just part of the of the documentation on the object. I suggest the above as a general criterion, though it may, admittedly, be rather a vague one. However, most reference materials are likely to satisfy one or more of the following functions, which are therefore suggested as specific criteria for inclusion.

- a. They may be used in the identification of unknowns.
- b. They may be used in the identification or measurement of various properties or characteristics of materials, e.g. origin, method of manufacture, "fingerprinting" parameters, changes undergone with time.
- c. They may be used to standardize quantitative measurements and/or instrumental techniques.
- d. They may be materials considered important because of well-defined associations with a time, place, school, individual artist, etc.
- e. They may form a record of materials in contemporary use, either for conservation or for the creation of artifacts.
- f. They may be used in connection with teaching.

Information

In general, three kinds of information are needed about a reference specimen.

- a. What it is.
- b. What it is intended for.
- c. What is the status of information about it that justifies calling it a "reference material".

I feel that, to be of much use, the Reports should

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try to bring out some information about the function and the status of our knowledge about a specimen. Merely publishing lists of pigments, dyes, fibers etc. without this kind of information would be of limited value. Also we might try to "upgrade" reference collections by encouraging the collection of things that will really support practical research, rather than the collection of a lot of samples about which one knows little or nothing.

An accompanying paper by J.A. Mosk draws a useful distinction in specifying differences between "standard materials," "standard objects," and "example materials", and this should be a practical starting point for defining the "status of information" about a reference material. However, primary classifications used by most laboratories are likely to be based on the nature of the material, i.e., on (a) above.

Provisionally, therefore, I propose the following.

1. Reference materials should be primarily grouped in some agreed listing of material categories.
2. Within a category, materials should be organized where possible according to systematic chemical, mineralogical, biological etc. nomenclature.
3. The report should state the purpose for which the materials were collected and the basis on which the reference status rests. The comments by Mosk may be taken as a starting point here. Although a reasonable amount of detail might be expected, very often it can be supplied for large numbers of items taken as a block.

Ultimately, perhaps, a coding system might be devised which would carry the information under (3) very concisely. However, further progress needs to be made on classifications before this would be feasible.

References

- (1) R.J. Gettens, "Preliminary report on reference materials". ICOM Report 69/10, Amsterdam 1969.
- (2) S. Rees Jones, "Radiographs and infrared photographs of paintings and objects in galleries and other institutions". In ICOM Report 14/72/1, Madrid 1972.

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SOURCES OF REFERENCE MATERIALS FOR
MUSEUM LABORATORIES

John Winter

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

SOURCES OF REFERENCE MATERIALS FOR MUSEUM LABORATORIES

John WinterAbstract

Some sources of reference materials likely to be useful to museum laboratories are listed, with a bibliography for access to further information.

Introduction

This listing is a first attempt at a guide to reference materials that are both generally available and of interest to workers in museum laboratories. As such it is inevitably very incomplete. The criterion of "general availability" is intended to exclude samples that were prepared for circulation to a restricted group of research workers or for some specific purpose, or collections of specimens in institutions and the like. The criterion "of interest to workers in museum laboratories" is a rather indefinite one, and some colleagues may well find a need for materials sold by the listed organizations but not specifically mentioned by type. However, some sources are given for qualitative reference materials or "example materials" (cf. paper to this meeting by J.A. Mosk) as these are believed to be of interest. In including them, the guide, and indeed the Reference Materials Working Group, is taking a broader view of reference materials than is the case with most national standards organizations, for example.

The guide is divided into three sections, corresponding to chemical analytical standards, to those for other kinds of measurement and to example materials. Where a source has materials appropriate to more than one section, it is listed in the one where the majority of its refer-

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ence materials seem to belong, with a cross-reference in the other. Each source listing consists of the name and address of the organization, followed by a brief indication of the types of material concerned (analytical standards for metals are indicated by the chemical symbols for the metals), followed by any further relevant notes.

Such materials as very pure elements and compounds, often used in chemical analysis, are excluded. A list including these would be extremely long; by the same token few people will have difficulty in obtaining them.

I hope to be able to update this list at subsequent Committee for Conservation meetings. To do so requires input from other members of the Committee. Please send information on any reference materials you think are interesting, from any country of the world, to the name and address at the head of this paper.

"References" in the entries below are to the bibliography that follows the main listing.

STANDARDS FOR CHEMICAL ANALYSIS

All-Union Scientific Research Center of the State Service for Standard Samples, All-Union Scientific Research Institute of Metrology, Sverdlovsk Branch, U.S.S.R.

Cu + alloys, Fe, Sn, Zn, various ores and minerals.

Above address is most complete available. See refs. 4, 6.

Alpha Analytical Laboratories,

57 Freeman Street, Newark, N.J. 07105, U.S.A.

Au, Fe, Pb + alloys (incl. Pb-Sn solders), Sn + alloys, Fe ores.

Catalogue available.

British Non-Ferrous Metals Research Association,

Euston Street, London, NW1 2EU, G.B.

Cu + alloys.

See ref. 4.

Bundesanstalt für Materialprüfung,

D-100 Berlin 45, Unter den Eichen 87, Germany.

Cu + alloys, Fe, Pb + alloys, Sn, Fe and other ores, glasses.

See ref. 4.

Bureau of Analysed Samples, Ltd.,
Newham Hall, Newby, Middlesborough, Teesside, G.B.
Cu + alloys, Fe, Pb + alloys, Sn + alloys, Fe and other ores.
See ref. 4.

Centre de Recherches pétrographiques et géochimiques,
15, rue Notre Dame des Pauvres, Case Officielle No. 1,
54500--Vandoeuvre-lès-Nancy, France.
Glasses, minerals.
See refs. 2, 4.

Centre technique des Industries de la Fonderie,
44, Avenue de la Division Leclerc, 92310--Sèvres, France.
Cu + alloys, Fe.
See refs. 2, 4.

CKD Praha,
Research Institute, Na Harfe 7, Praha 9, Vysocany,
Czechoslovakia.
Cu + alloys, Fe.
See ref. 4.

Department of Energy, Mines and Resources,
Mineral Sciences Division, 555 Booth Street, Ottawa K1A
OG1, Ontario, Canada.
Cu alloys.
See ref. 4.

Fédération européenne des Fabricants de Produits
réfractaires, 44, rue Copernic, 75016--Paris, France.
Minerals.
See refs. 2, 4.

Institut de Recherches de la Sidérurgie française,
185, rue du Président Roosevelt, 78100--St. Germain-en-
Laye, France.
Fe, Fe-containing minerals.
See refs. 2, 4. Also distribute samples from the Centre technique
des Industries de la Fonderie.

Institut du Verre,
34, rue Michel Ange, 75016--Paris, France.
Glasses.
See ref. 2.

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Iron and Steel Institute of Japan,
Keidanren Kaikan (3rd floor), No. 5, Ōtemachi-1-chōme
Chiyoda-ku, Tokyo 100, Japan.

Fe, Fe ores.

See ref. 4.

Mueller Brass Co.,
Port Huron, Michigan 48060, U.S.A.
Cu alloys.

National Bureau of Standards,
U.S. Department of Commerce, Washington, D.C. 20234,
U.S.A.
Cu, Fe, Pb, Sn, Zn and their alloys, electron probe standards
(Au-Ag, Au-Cu, Cu-Zn, Fe-Si), various ores, minerals, glasses,
isotope ratio standards.
Catalogue: NBS Special Publication 260. Further details in ref. 4.

Research Institute for Ferrous Metallurgy,
Budapest XI, Fehérvári Ut 130, Hungary. (Export:
Metalimpex, 1051 Budapest 5, Münnich Ferenc Ut 9-11,
Hungary).
Fe + ores.
See ref. 4.

South African Bureau of Standards,
Private Bag X191, Pretoria, South Africa.
Au.
See ref. 4.

Tyseley Metals Ltd.,
Kings Road, Birmingham B11 2AU, G.B.
Cu alloys (Cu-Sn, Cu-Zn).
Information from company.

Zinc et Alliages,
34, rue Collange, F-92 Levallois-Perret, France.
Zn + alloys.
See ref. 4.

Also:

Polysciences, Inc. (see below).
X-ray microanalysis standards.

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STANDARDS FOR OTHER MEASUREMENTS

Duke Standards Company,
445 Sherman Avenue, Palo Alto, California 94306, U.S.A.
Granulometry (microspheres and various other particles of known sizes).
Information bulletins from company.

Munsell Color,
Macbeth Division of Kollmorgen Corporation, 2441 North Calvert St., Baltimore, Maryland 21218, U.S.A.
Munsell color standards.

Polysciences Inc.,
Paul Valley Industrial Park, Warrington, Pennsylvania 18976, U.S.A.
Microscopy calibration and resolution standards, granulometry (microspheres and other particles of known size).
Catalogue available.

TALAS,
Division of Technical Library Service, 104 Fifth Avenue, New York, N.Y. 10011, U.S.A.
Textile fading cards, grey scale.
Company deals mainly in conservation supplies. Catalogue available.

Also:

All-Union Scientific Research Center of the State Service for Standard Samples (see above).
Colorimetric atlases (several).

Bundesanstalt für Materialprüfung (see above).
Corrosion test samples (ferrous and non-ferrous metals), color reference samples.

Cargille, R.P., Laboratories, Inc. (see below).
Refractive index standards (liquid and solid).

National Bureau of Standards (see above).
Color charts (ISCC-NBS Centroid), fading test papers and plastic chips, granulometry (microspheres), radiocarbon dating reference, scanning electron microscope test specimen, X-ray and photographic step tablets, X-ray diffraction internal standard.

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QUALITATIVELY KNOWN MATERIALS

Cargille, R.P., Laboratories Inc.,
55 Commerce Road, Cedar Grove, N.J. 07009, U.S.A.
Furs, hairs and other fibers (as slides), minerals (in bulk or as slides), starches (as slides).
See data sheet RS-450.

Conservation Center,
New York University Institute of Fine Arts, 1 East 78th Street, New York, N.Y. 10021, U.S.A.
Pigments (set of 29).
These pigments are no longer available from National Bureau of Standards.

Paxton, Frank, Lumber Company,
5701 West 66th Street, Chicago, Illinois 60638, U.S.A.
Woods (set of 46).

Rocks and Minerals,
4 Royal Crescent, Cheltenham, Gloucester GL50 3DA.
Minerals, rocks, microscopic sections.

TAPPI Fibrary,
The Institute of Paper Chemistry, Box 1048, Appleton, Wisconsin 54911, U.S.A.
Papermaking fibers.
Catalogue available.

Ward's Natural Science Establishment, Inc.,
P.O. Box 1712, Rochester, N.Y. 14603, U.S.A.
Minerals, rocks, soils; thin sections available.
Catalogue available.

Wide World of Herbs, Ltd.,
11 St. Catherine Street East, Montreal, H2X 1K3, Canada.
Natural dyes, various other botanical products.
Catalogue available.

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TEXTILES

Coordinator : J.H. Hofenk-de Graaff (Netherlands)
Assistant coordinator: M. Flury-Lemberg (Switzerland)
Members : A.J. de Graaf (Netherlands)
S. Landi (U.K.)
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G. Vial (France)
M.C. Whiting (U.K.)

Programme 1975-1978

1. The conservation, restoration and analysis of textiles (Socorro Mantilla de los Rios, Flury-Lemberg, Landi).
2. The influence of washing agents on the deterioration of ancient textiles (Masschelein-Kleiner).
3. The analysis of natural dyestuffs in ancient textiles (Masschelein-Kleiner, Hofenk-de Graaff, Whiting).
4. The ageing of natural fibres (De Graaf, Schaffer).
5. Technical studies on weaving of ancient textiles (Vial).
6. Promoting better contacts between other groups which are working in the field of textile conservation, like the Centre International d'Etude des Textiles Anciens, The Irene Emery Round Table and the ICOM - Costume Committee (Hofenk-de Graaff, Flury-Lemberg).



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THE ESTABLISHMENT OF A TEXTILE
CONSERVATION CENTRE IN BRITAIN

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5th Triennial Meeting
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THE ESTABLISHMENT OF A TEXTILE CONSERVATION CENTRE IN BRITAIN

Karen Finch

Museums acquire the objects in their collections in many ways including purchase and bequests. Most of these objects, certainly those most regularly on public show, are of immediate cultural or artistic significance. Museum authorities are expected to exercise control over the objects in their care and to decide what shall be exhibited and the conditions and circumstances under which this shall be done, what shall be kept in reserve or retained especially for research and, in the context of this paper, what objects shall receive conservation treatment.

In Britain many of the great museums have their own conservation departments where such treatment can be given but other, smaller museums, may have to avail themselves of special workrooms set up by an Area Museum Service or some other accredited conservation service. This is the situation at present but it has not always been so. Moreover in Britain, as in other countries, not all historic objects of cultural and artistic importance are in museums and the care of these pieces may be spread amongst a number of people and authorities.

While the objects themselves may be of the highest national or even international importance, there is no guarantee that this will be recognised by those with ultimate authority over them and this fact could put the safety of the objects at risk especially if their custodians are not conservation-minded or have other, to them, more important priorities. If the objects in question are textiles, then the situation becomes even more serious. I would like now to come from the general to the particular and explain how this situation has been dealt with in Great Britain over the last thirty years of which I have personal knowledge and during which time I have been personally involved.

Great Britain has an enormous heritage of historic textiles many of which are to be found in Great Houses, places of worship, public buildings and in private ownership. The reasons for this are varied - the wealth of those who, in the past, built and furnished beautiful houses and were able to maintain them, the fact that there has been no major fighting for many centuries on British soil and the long connection that the British have had with textiles, not only those produced by their own manufacture but also imported from abroad.

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Interest in things past has grown steadily as people have been able to move around and visit other parts of their own and other countries and amongst the greatest tourist attractions in Britain are the country houses thrown open to visitors and in these houses may be seen a great many textiles. Each house is, in its way, a museum, but has the added dimension of holding up a mirror to the home life of the family who owned and occupied the house, reflecting the life and interests of that family through the contents of the house with its examples of differing tastes and times in a way that the more formal arrangements of a museum could not do.

Many of these houses are now owned by the National Trust - not, as its name might suggest, a State Department but, in fact, an organisation funded entirely from membership fees or special appeals and bequests and any money brought in by the entrance fees to their houses. Some houses are still privately owned, even partly occupied by their owners who seek to offset the cost of their upkeep by charging for entrance to the houses, gardens and any other attraction which they can provide - in fact the Stately Homes business has almost become an industry with the aristocratic owners vying with each other to attract more visitors. This situation raises a number of difficult preservation problems. While such houses were private residences, their upkeep was in the hands of the owners who with their guests were the only people who used them.

Most owners felt a responsibility to their family and its history and a great pride in their possessions and, as a consequence, the estates, including the houses and their contents were kept in excellent order. The well-trained and numerous staff employed housekeeping techniques in the care of the interiors of these great houses which was preventive conservation in actual practice. Unfortunately for the safety of the contents of such houses, the times changed - it was the end of an era and the financial burdens of such houses and estates, and the difficulties of finding and paying skilled staff resulted first in the depletion of staff and other economies and then the realisation that it was no longer possible to carry on in any way which would keep the house and its contents intact and often such properties were offered to the National Trust. Alternatively, owners decided to remain as long as possible but to open the houses themselves to the public and hope the entrance fees might help to maintain the property.

The effects of opening the houses - often for long periods - were not immediately apparent except in welcome revenue but gradually those in charge became aware of the

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deterioration of the contents - particularly the textiles - through the exposure to light and variations of temperature and humidity. This awareness became known about the same time as it also became apparent that visiting a Great House was a tourist attraction which was increasing in its appeal. Deterioration, once begun, accelerates at an alarming rate and textiles, fragile and of some age, can quickly become unsightly. If the custodians of such places were aware that the textiles were beginning to fall apart, the visitors noticed too and many felt that they should be able to do something to help save these precious fabrics.

May I go back a little in time now and explain how I and, eventually The Textile Conservation Centre of which I am now the Principal, fit into this situation.

From 1954 to 1959 I worked at the Victoria and Albert Museum in what was then known as the Art workroom at first on tapestry conservation/restoration but later my job entailed the cleaning and preparation of textile objects for display in the Museum.

My background of Danish training in weaving and design and some knowledge of the attitude to conservation in Denmark, made me interested in the many new ideas being put forward in the field of conservation but I was not, at that time, prepared to devote my life to this particular aspect of what was then an interest in all textiles in a very wide sense. Looking back on events I am amazed at the way that different threads of what seemed then a sequence of unrelated happenings have woven themselves into the situation we have today.

In 1959 I decided to leave the Victoria and Albert Museum to continue exploring my interests in my own home where I could be with my family. As soon as I had left the Museum, I was approached by those who had become concerned at the deterioration of textiles in their care with requests to treat these pieces, some came from National Trust houses, some from private owners, all were directed to me by the Victoria and Albert Museum. Other museums with no textile conservation departments of their own brought their problems to me too, and in a very short time, I was literally inundated with requests to conserve textiles. These were of all kinds, some of great value historically and artistically, some had sentimental value to their owners only but all needed treatment. I was able to gather together a group of associates who, under my training and direction, worked on the pieces brought to me.

Before too long, I was being approached by an increasing number of people from many different countries who wished to study the conservation of textiles and, although I could offer no set syllabus or organised training, many of those who studied with us in my private workroom went on

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to hold positions of importance in various museums all over the world.

During the 16 years that we studied, practised, and taught textile conservation in this way, we found it necessary to make many decisions regarding methods and the desirability of following some of the new ways of treating degraded textiles and we ourselves became innovators in some respects. At every opportunity I read reports of the work of others in the field and, most valuable of all, met and discussed with them at as many conferences, seminars, lectures and meetings as time and money permitted me to attend.

In 1964 at the International Institute for Conservation Delft Conference on Textile Conservation, I gave my first paper on the training in textile conservation.

I began to have a formal connection with a course in the History of Dress which was being run by Stella Newton at the Courtauld Institute of Art, which is part of London University, giving the students on that course an insight into fibres, dyes and finishes of fabrics, the reasons for their deterioration and a general idea of how they might be preserved by preventive and active conservation methods. Preparation of the lectures for this teaching was responsible for decisions in my own mind regarding exactly how I saw the structure on which a properly organised course in Textile Conservation could be run.

Meanwhile the work of actual conservation continued to pour into my home which we had already had to change for a larger house in order to have more space. Other commitments too came one in the form of a request in 1969 for me to do a survey at Knole Park, one of the historic houses where there are an enormous number of old and valuable textiles.

The survey was to be a comprehensive one with a report on every textile on display in this large house, together with an estimated cost of conservation should that be possible. As I could only visit spasmodically when time permitted I was able, over the two years period during which the visits took place, to observe at first-hand the rate of change in the condition of the textiles. Knole Park is almost in the town of Sevenoaks in Kent, near to London and with one of the highest number of visitors of all the great houses. The textiles are subjected to all the dangers that attend the opening of such a house to the public.

Perhaps the most important textiles amongst the large collection are the hangings of a State Bed - the

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so-called King's Bed. The bed-curtains and the coverings of the furniture en suite in the room are of a triple-weave fabric of gold and silver brocade sometimes known as Lampas. The curtains are lined with carnation pink silk, embroidered with silver, all edged with heavy gold fringe with black and carnation pink silk and gold tassels. The coverlet and head-board in the same material are embroidered in gold raised work. Earlier repairs had been done to the gold and silver brocade through the linings and the repairs themselves were now disintegrated and no longer able to support the heavy weight of the metal threads. I was distressed at the further damage that I could see on the fabric on each visit and pressed for something to be done but I knew that even if enough money could be raised, my limited work-force could not undertake the task for it would mean that they would be tied up, doing very monotonous work for many years. Nevertheless, I gave the matter a great deal of thought and realised that if I could devise a simple way of stitching the cleaned brocade onto a strong supporting material so that the design of the brocade would not be lost, then the image of the beautiful old fabric could be saved.

I took one stool-top, cleaned it, and then mounted it onto a suitable man made fabric of the right colour and weight, and by trial and error, devised a method of restoration which was within the capabilities of any good needlewoman, provided that there was proper supervision to maintain the correct method. Cleaning of historic textiles should, in my opinion, always be the province of professional conservators but the method of restoring the textiles of the Kings Bed at Knole by sewing was a chance for all those volunteers who, distressed as we all were at the condition of the beautiful textiles and anxious to help, could do just that. The task of restoration of the hangings of the Kings Bed will take many years of repetitious work but nevertheless the response to an appeal for volunteers was startling even although I am sure most knew what they were taking on.

A workroom was set up at Knole Park which is now supervised by the Conservation Department of the Victoria and Albert Museum because the Kings Bed belongs to the Treasury and is their responsibility.

In the more than 30 years that I have been working on the historic textiles of Britain, this is the only time that I have been able to advocate that large numbers of volunteers untrained in conservation could safely be set to work on textiles of historic significance. I feel there are many other areas in which small groups of volunteers may play significant roles - provided the necessary professional supervision is available.

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In order to take advantage of all the help that has been so generously offered to the Textile Conservation Centre we had occasion to draw up our definitions of the meaning of the words commonly used by the Textile Conservation Centre to describe our work and relationship with our volunteers and they are as follows.

CONSERVATION - RESTORATION - MAINTENANCE

CONSERVATION as a general term may be used to cover a number of different forms of treatment.

CONSERVATION is concerned with the safe-keeping of objects as examples of their kinds and periods.

Conservation treatment must neither add to nor take away from the original but only make it safe for display, storage or future study.

RESTORATION aims to make objects look and function according to the intention of their original makers by reproducing worn or missing parts with new materials. Traditional workmanship may or may not be used.

MAINTENANCE
OR
PREVENTIVE
CONSERVATION means to keep and support objects in any particular state so that they do not suffer or their condition decline, by providing good conditions (i.e. a clean controlled climate, and protection from light) with constant supervision.

REPAIR AND
RENOVATION may prolong the functioning capacity of an object by removing or altering unwanted parts and substituting worn or missing parts with pieces from another object.

CONSERVATION
TREATMENT is applied to Historic Textiles -
on public display
in reserve collections or storage
in private collections where they are available for study and research but not otherwise seen by the general public.

Many different fibres, dyes and construction techniques have been involved in producing these textiles and their survival depends largely on the professional training and scientific knowledge possessed by the people responsible for their care and conservation.

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STUDENTS accepted on the Textile Conservation Course which the Centre runs in conjunction with the Courtauld Institute of Art, are required to hold a University degree in either Art or Science. On the course, they are taught to recognise the composition of each type of object, the fibres, dyes and constructional techniques, and then in a scholarly and scientific manner to research, record and choose suitable reversible conservation methods and materials.

The aim of those working, advising, teaching and studying at the Textile Conservation Centre is to endeavour to keep safe all aspects of objects made wholly or in part from textiles, including the preservation of their history, and the techniques by which they were made whether that information is already known or is revealed by examination, research or during treatment.

RESTORATION is applied to objects still in ordinary use and where the design is an integral part of the fabric, as in the dark coloured areas of tapestries and carpets. When the composition of the design has disintegrated along with the oxydised remains of the black or brown weft yarns, the white warp yarns will be exposed with consequent distortion of the design. This may be remedied but other restoration techniques are not normally used at the Textile Conservation Centre because restoration of textiles is costly and - in the long term - rarely successful.

There are several reasons for this lack of success. In the visual sense one reason is that artists and craftsmen of one age do not share the ideals of another age and restoration would inevitably interfere with the designer's original intentions and cause the object to cease to be a statement of its own time.

In the practical sense another reason is that the many variables involved in the production of yarns and dyes and their rates of fading and decay may have the effect of changing apparently successful restoration into damage after a few years.

APPRENTICES in practical tapestry conservation at the Textile Conservation Centre are required to hold an Art College degree or diploma to ensure the necessary informed understanding and sensitivity to colour and design principles

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in this essentially pictorial branch of textile conservation.

MAINTENANCE

or GOOD HOUSEKEEPING practices provide the foundation for the continued existence of any object left to us from the past. Given sound maintenance practices, the time-consuming, and therefore expensive, work of conservation may be postponed and perhaps not become necessary for many years, though it must be considered that the long term survival of any textile object kept in open conditions is problematical.

REPAIR AND
RENOVATION

techniques are used to maintain furnishings and curtains of no great age or intrinsic merit, so that they may continue to provide the setting for other objects of historic value.

It is on the quality of the daily maintenance that much of our national - and international - heritage depends and this is an area where voluntary work by disciplined hands and informed minds may be welcomed and put to good use.

Lack of professionally trained guidance combined with inexperience sometimes results in an inability to evaluate the size and complexity of a project. Consequently damage has been caused and volunteer groups would be advised to work only under the supervision of trained conservators.

We, in the Textile Conservation Centre, believe that the aims of volunteers in offering their time and services are the same as those of professional conservators, namely to save those objects of the past which are considered important.

However, in regard to textile conservation, it may be necessary to establish a code of practice agreed to by all concerned or the efforts of volunteers may result in damage rather than conservation because of the extreme vulnerability of old and fragile textiles.

It is essential that volunteers should be willing to accept instructions and carry them out with an unfailing sense of responsibility and integrity.

Organisers of any large-scale voluntary undertaking should recognise that difficulties can arise. Members taking part may have other commitments which could over-ride their voluntary activities. This can make it difficult to command adherence even to apparently agreed arrangements.

Should disagreements occur in any voluntary scheme involving textile conservation, the standard of work will,

inevitably be affected. A project which attracts volunteers but which is, nevertheless, labour-intensive, cannot afford to lose its attraction, otherwise the unpaid labour force will not remain until the work is complete.

It would be a pity if the vagaries of fashionable ideas, the pressure of the times in which we live or the difficulty of maintaining a happy atmosphere over a long period of repetitive work requiring a high standard of achievement were to be the decisive factors in whether National treasures are to be lost or saved for the future.

It would also be a great loss if the profession of textile conservator failed to attract, train and retain in employment the right type of person because of confusion about what can reasonably be expected from volunteers and what is the province of the fully trained textile conservator.

What then are the areas in which volunteers can be of assistance?

Broadly speaking, we think that volunteers can best be used in preventive conservation, such as in preparing and helping with the organisation of opening a house to the public.

1. by fitting visually acceptable blinds and curtains to fit in with existing surroundings and by seeing that they are used to exclude light whenever possible.
2. by making stylistically suitable loose covers for upholstered furniture so that these can be left on even during visiting hours except for allowing one chair or sofa to be uncovered, in rotation.
3. by making case covers for the protection of bed-hangings and tapestries.
4. by making drugget or baize covers for important carpets.
5. by making sure that special carpets or covers are provided for visitors to walk on so that the grit and dust from their foot-wear does not damage the more precious pieces of floor-covering.
6. by cleaning and keeping clean and free from pests, the surroundings of textile objects - furniture etc.

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7. by preparing important objects for storage either for the period of seasonal closure of the house or to await professional conservation treatment.
8. by giving general maintenance and repair to replacement and supporting textiles such as loose covers, blinds and protective curtains.
9. volunteers who have had instruction in the principles of preventive conservation can assist in the care of the contents of a house by looking for and devising ways to minimise the damage which can be caused by environmental conditions - light, variations of temperature and humidity, static electricity, handling of objects etc. and, with personal contact and knowledge of the conditions of the house, can help to overcome these hazards.
10. by fund-raising.

The Textile Conservation Centre itself is grateful for receiving voluntary help for secretarial work, typing, filing, photography, for cataloguing the library and study collection and for special research when needed.

Experts in various fields are helping with objects belonging to organisations in which they are personally involved and which require repetitive time-consuming conservation treatment and with the sometimes equally time-consuming documentary aspects of our work.

It is important to preserve the unique aspects of each of the great houses of Britain. Museum collections may, legitimately, be used to achieve the idealised look of fashion plates - whether they are of dress or interior design - but, for a great house to have meaning in the fullest sense as a monument of its past it should remain as when it was lived in, because it is often only the organic growth of the contents of these houses and their associations with the people who lived there, that gives meaning to an individual object and its place in time.

One of the most important and worthwhile areas in which volunteers, especially those with an interest in history, can help, is by doing research and documentation on the objects on view. This is very time-consuming and therefore expensive work, but the results of such research, incorporated in the guide book, would add greatly to the understanding and knowledge which a visit to a great house can give.

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Realisation of the enormous problem of conservation of textiles in Great Britain outside those in museums and the need for training so that there would eventually be sufficient qualified conservators to deal with this problem, came gradually over the years.

By 1971 both I and my associates were convinced that these dual needs could be satisfied only by the setting up of a Centre for the Conservation of Textiles and an associated training scheme at university level. We prepared and circulated a Memorandum, setting out the problems and our ideas for their solution. The reaction was impressively favourable and we then went ahead to translate our ideas into concrete proposals.

We received the greatest help and encouragement from our friends and colleagues in Britain and all over the world whom we approached for help and advice. They responded most generously with explicit details of the equipment, costs and organisation of their own conservation departments. We made plans and lists and did costing and estimating so that we were able to satisfy all who asked that we had a proper understanding of all that would be involved and the will and ability to carry out our intentions.

We ceased to accept any more conservation jobs in September 1971 and concentrated on working our way gradually through the backlog of work accepted before that date. We were glad to be able to keep our team of associates together but wondering about the future and then, almost overnight it seemed, in the Spring of 1975, a great many events happened almost simultaneously.

We were offered suitable premises for the Centre at Hampton Court Palace, our company was registered and then received the status of a Charitable Company and this enabled us to receive grants and other help from Trusts and from the Crafts Advisory Committee to buy equipment. The Crafts Advisory Committee is a Government sponsored body which is still giving us much needed and appreciated grants towards the training of our students.

The Textile Conservation Centre was a reality.

Already we were running pilot courses in Textile Conservation in conjunction with the Courtauld Institute which is part of London University and these courses moved, as we all did, to the Hampton Court premises. The last of these pilot courses finished in the Summer of 1977 but it is hoped eventually to recommence with a permanent three year post-graduate course.

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In textile conservation, experience is as necessary as initial training so the course has been designed to provide as sound a basis of knowledge as possible on which the newly qualified conservators can build their future experience and study. The work of conservation at the Centre continues. Some of our former students have stayed and the staff is growing. The Centre already operates in three departments - teaching, general conservation and tapestry conservation and runs two other courses besides the Textile Conservation Course. One is a one-year course for those already employed in museums and students are sponsored by their place of employment to which they are expected to return, and the other a three-year in-service course in tapestry conservation.

The Museums Association has recognised the Textile Conservation Centre as a training institution.

The generosity of the Leverhulme Trust is enabling us to engage a scientist to work with us and study our special problems, we are very grateful because we believe that sound decisions on the most suitable treatment for specific purposes can best be achieved through the combined knowledge and understanding of the Textile Arts Historian, the trained conservator with experience of textile and conservation techniques and the scientist, who can evaluate the causes of deterioration of an historic textile.

The Centre's connections with the Textile Department of the Victoria and Albert Museum enable us to work closely with historians of dress and textiles, our relationships with other conservators enable us to exchange views and to consult - and be consulted on many varied problems - soon our new science department will enable us to complete the triangle of Historian - Conservation - Scientist.

Our Scientist will be expected to take an important part in the teaching of the Centre and to liaise with others, who are doing conservation research in our field. He, like the rest of us, will need to be as constantly aware that new knowledge precipitates new questions and new problems, even perhaps fundamental changes in our approach.

For instance - a costume historian doing research into the patterns and making up of historic costume may confirm our belief that we should do only the most essential work consistent with putting an object safely on show - with the accent on safely - but supposing the main reason for an object being preserved is its flamboyant and spectacular quality, which must be kept intact if it is to arouse interest and be understandable and attractive to members of the general public who want to see an object as it appeared to members of the public when it was in use.

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Such an approach may however lead to questions which will require much deeper analysis of any given problem, than has been faced before or we may lose the integrity of unique pieces as historical documents for study and research. We hope that our training will help to turn out responsible textile conservators who with knowledge and understanding may work objectively with Historians and Scientists to resolve such problems.

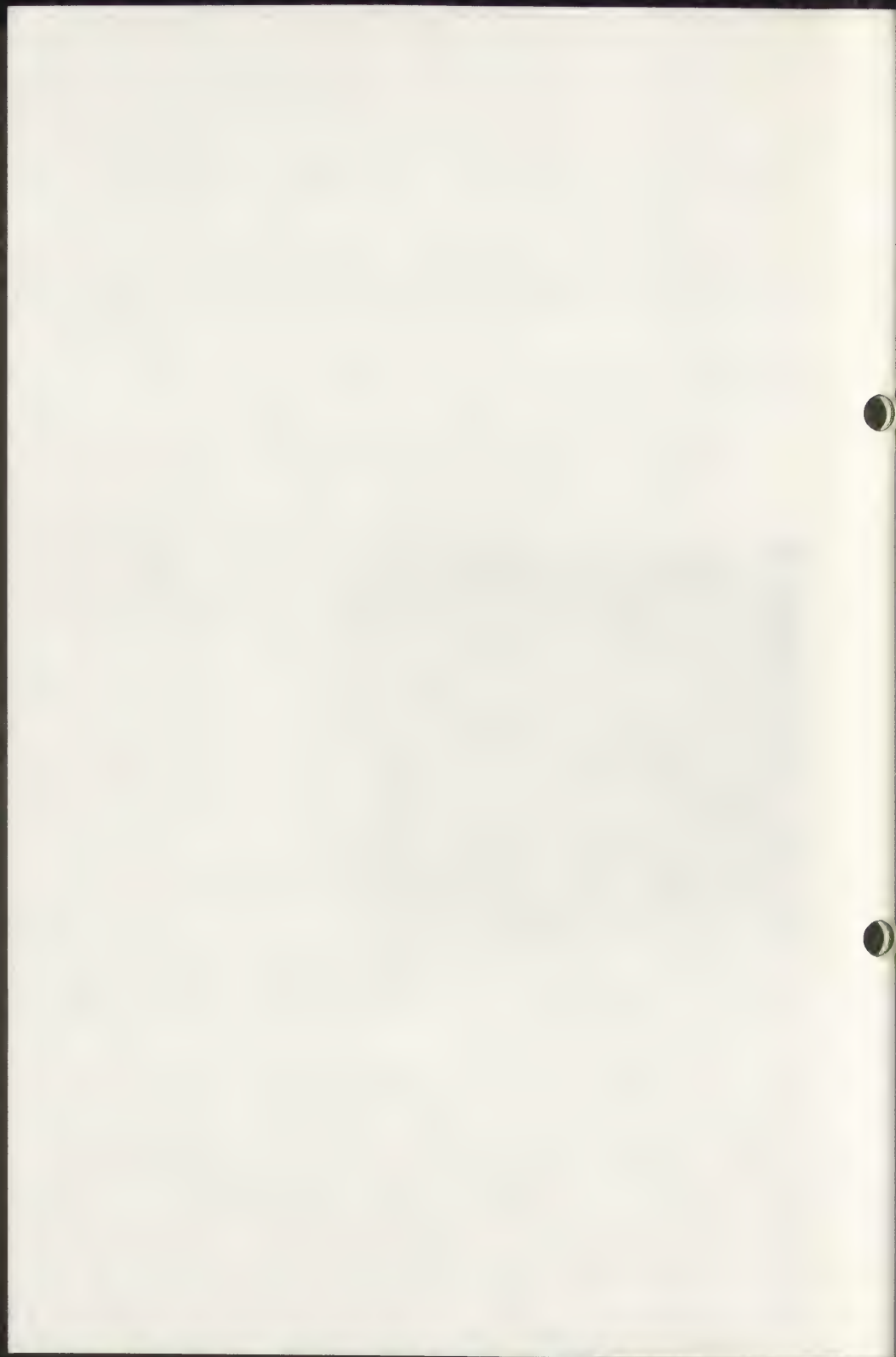
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THE IDENTIFICATION OF DYES IN
OLD ORIENTAL TEXTILES

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

THE IDENTIFICATION OF DYES IN OLD ORIENTAL TEXTILES

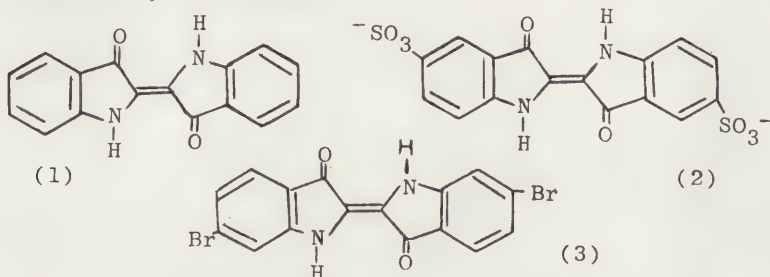
M.C. Whiting

The dyes present in oriental carpets and related textiles can often be identified by extraction from the fibre, liquid-liquid distribution, and measurement of the visible absorption spectra. Madder and indigo present no problems. Cochineal and lac are difficult to distinguish either in this way or chromatographically, and some samples may have been mis-identified in the past; a reliable procedure is now available. Yellow dyes are usually flavanoid, and thin-layer chromatography is necessary for chemical identification; even then, the botanical source may not be evident. Early synthetic dyes can usually be identified as to chemical type on a small scale by simple tests, and actual constitution determined by mass spectrometry. Useful conclusions about date and place of origin of a textile can often be reached by these means, and generalisations made about the dyeing techniques of particular groups.

The identification of the dyes of natural origin used in early oriental carpets and similar textiles should assist in solving problems of attribution and dating. The same is true for some textiles of the period 1860-1900 (say), which retain, wholly or in part, the aesthetic merits of earlier pieces, but incorporate early synthetic dyes, often very sparingly. Our work began in 1971 independently of that of Hofenk de Graaff and Roelofs,¹ but since 1974 has benefited from interchange of information with the Amsterdam group. In some respects it has taken a different and complementary course, with more emphasis on liquid/liquid distribution and spectroscopic methods. We have aimed at a firm chemical identification with 1 μ g. of dye, usually found on ca. 1 mg. of fibre. It will be convenient to group dyes by colour, taking natural and early synthetic dyes together because one should avoid, whenever possible, the assumption that the piece examined was made at the date implied by the design.

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(1) Blue dyes are usually indigotin (1), which is extracted from water by methylene chloride at all acidities, and then has



an absorption maximum at 600 nm. It can be identified by thin-layer chromatography on 10% acetylated cellulose, but disappears rapidly from the plate. In oriental textiles it can be assumed to originate from Indigofera species, grown in India, or (after 1891) to be synthetic; in either case it is quite pure, so chemical identification affords no proof of date. Indigotin remains the blue dye most commonly used, well into C20. As indigo was also used in all countries from C16 onwards, no conclusion as to place of origin can be drawn. There are a number of other plants which contain precursors of indigotin, e.g. woad (Isatis tinctoria L.) in temperate Europe, and may have been used in dyeing.

Other blue dyes encountered are

(i) Indigodisulphonic acid (2), found in an Indian carpet bought new in 1883, and in a typical late C19 Kurdish runner. This dye shows properties typical of acid direct dyes, i.e. is not extractable by methylene chloride from water, but becomes so when large organic cations, such as tetrabutylammonium salts, are added. It can be identified by its absorption spectrum and, if necessary, rigorously proved by methylation with methyl fluorosulphonate and mass spectrometry.² Indigodisulphonic acid is called "extract of indigo" in the early literature. It was made from natural indigo, by treatment with concentrated sulphuric acid, long before indigotin was synthesised, was first described in 1740, and in oriental textiles seems to have been the only popular alternative to indigotin. However, elsewhere it was displaced around 1900 by

(ii) Cationic blue synthetic dyes of several types, e.g. Spirit Blue (4) and Methylene Blue (5). These also are non-extractable from water with methylene chloride, but they become extractable on adding large organic anions,

e.g. salts of naphthalenesulphonic acids. They became available in 1860-1880, and are too numerous for identification by guessing and comparing visible spectra; they do, however, give good mass spectra, from which their constitution can be deduced.

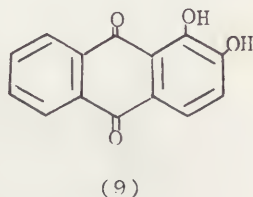
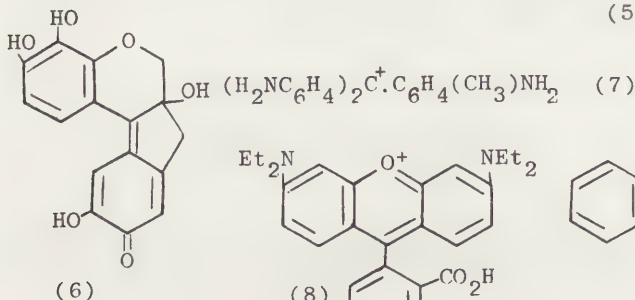
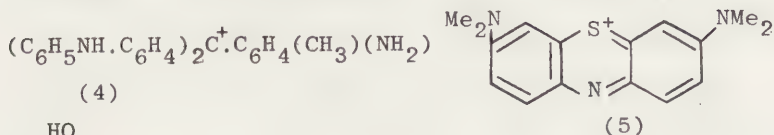
(iii) Sulphonated derivatives of the above, which were easier to apply to fibres, and were reported around the same period; and

(iv) Complex anionic azo-dyes, extractable in the presence of large cations. One apparent fake of a "Holbein" carpet contained a dye of this type, but we have not otherwise encountered dyes of groups (iii) and (iv) and cannot comment on their exact identification.

Tyrian Purple (3) has never been encountered in our work. Logwood (Haematoxylon campechianum), containing haemateine (6) once has, in a Turkoman bag also containing an azo-dye. It is extractable from water into ether, and is easily identified by giving a range of spectra at different pH values, notably at 444 nm (neutral), 520 nm (dilute acid) and 546 nm (dilute alkali; transient). In mass spectrometry the main peak is at m/e 302, not 300 as might be expected. Its detection, like that of the related brazil-wood,¹ is also satisfactory by thin-layer chromatography on 10%-acetylated cellulose. Logwood gives colours varying from blue to a bluish red, according to the iron/aluminium ratio in the mordant.

Magenta-coloured dyes usually prove to be fuchsine (of which one synonym, among many, is "magenta"). These are triphenylmethanederivatives of slightly varying composition, e.g. (7), and became available from around 1860; they were extensively used in the Caucasus, in Anatolia, in Persia and in East Turkestan, but have not been found in pieces thought likely to have been made in West Turkestan or Afghanistan. They can be detected by becoming extractable from water into organic solvents like methylene chloride when large organic anions are added, by decolorisation with sulphite, or by a colour-change toward green on adding strong mineral acids; exact identification requires mass spectroscopy. We have also twice encountered Rhodamine B (8) on two Turkoman rugs made by the Ersari tribe; this became available in 1883, and is especially easy to identify because of its spectacular fluorescence. One obtains the impression that bluish-red shades became available in azo-dyes of superior dyeing properties before 1900, and identification of fuchsine probably implies a late-C19 rather than a C20 date. Fuchsine fades badly on

treatment with alkaline solutions, e.g. soap.



Red dyes are of primary importance. Much the commonest is madder, which consists of a number of hydroxyanthraquinones, e.g. alizarin (9), extractable into ether from aqueous solutions, and easily identifiable chromatographically.¹ Madder is also easily identified, and can to some extent be analysed into its constituents,³ by partition and visible spectrometry. Kermes, though much discussed in the carpet literature, has never been encountered in any oriental textile; its coloured constituent kermesic acid (10)⁴ is extracted into ether in the same way as the madder quinones, and need not be confused with the other insect dyes with similar visible spectra. These are lac, containing a mixture of laccaic acids (e.g. 11), and cochineal, which when fresh contains pure carminic acid (12). They are important dyes, lac giving the rich red colour to classical Persian carpets, and of course constituting the main red dye of India, while cochineal is found in many Cl9 textiles. Lac and cochineal are almost impossible to distinguish by sight, and difficult to distinguish by thin-layer or paper chromatography,¹ in most systems remaining immobile or moving near the solvent front. They also give similar spectra in most solvents. We know of cases where cochineal has been identified in early Indian or Persian textiles; in one we were able to analyse a generous specimen and satisfy ourselves beyond question that lac was really present. (It seems improbable that much cochineal was in fact imported into these countries before domestication in the Canary Islands, and then the Mediterranean, from 1820 onward; although it probably did reach Turkey soon after it became common in

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Europe, around 1550.¹ An unsuccessful attempt was made to grow cochineal insects in arid parts of India early in the nineteenth century). In our early work, based on measurements of the distribution coefficient of the colour when solutions of the dye are shaken between ether and aqueous sulphuric acid, a distinction could be made for most specimens, because the usual laccaic acid mixture is moderately soluble in ether (ratio around 0.4 in ether to 1 in water), whereas carminic acid is not (ratio <0.1). This test was confirmed when samples were adequate by measurements of the shape of the spectrum in 50% sulphuric acid, and by the chromatographic methods described.¹ However, some old specimens of cochineal seem to contain transformation products of carminic acid which are more ether-soluble, while some specimens of lac contain less than usual quantities of ether-soluble material, so that both give intermediate values in the measurement of distribution coefficient. We have therefore evolved a better method. The aqueous solution of the insect dye, easily known to be such from its visible spectrum, is first extracted with ether to remove madder, if present, some of the lac constituents, and any degraded carminic acid. It is then extracted with pentan-3-one (diethyl ketone), and the distribution coefficient (solvent/water) is measured; lac gives a value above 1.4, cochineal about 0.9. As a bonus, in this solvent the shape of the absorption curves is usefully different, as shown in Fig.1. So far, this test has given completely unambiguous results every time it has been applied, even for samples of about 1 µg.

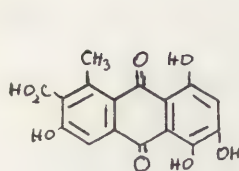
Red or orange azo-dyes are frequently encountered in textiles plausibly dated 1880-1900, many of which are important enough to be found in museum collections. At this period the synthetic dyes available were relatively simple and not extremely numerous, so that there is some prospect of identifying them; representative examples are (13-15). Rather surprisingly, the range of dyes encountered in one group, of piled textiles from West Turkestan, proved to be very limited, a substantial majority proving to be Ponceau 2R (13). Dyes already encountered can be recognised by visible spectra, of which each azo-dye gives four (in strong alkali, strong acid, neutral solution, and neutral solution in the presence of copper),⁵ so that accidental co-incidence was seldom a problem. To identify the dyes in the first place was more difficult, and required work on resonance Raman spectra,⁵ chemical degradation, and best of all, extraction into methylene chloride as tetrabutylammonium salts, methylation, and mass spectrometry. This work is being published elsewhere.^{2,5}

The Turkoman women who used the early synthetic dyes

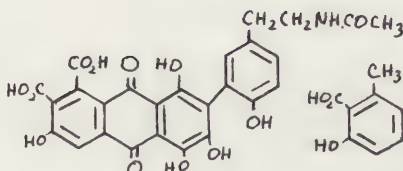
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seem to have treated them in a manner quite different from that of sophisticated dyers. In the first place, they used them very sparingly, often to the extent of less than 1% of the area of naturally-dyed fibre; thus the familiar assumption that synthetic dyes made the products cheaper or easier to make is certainly untrue for this period. On the contrary, they were probably so expensive at first that they had to be treated like silk, to emphasise small but important areas in the design. Ponceau 2R was also used, in perhaps slightly later pieces, as a substitute for one of the two tones of madder, in (minor) sections of the traditional designs where a lighter and brighter madder would have been employed, while a deeper or browner madder was retained for the ground. Ponceau 2R must have been thought of as equivalent to madder, and quite often is found double-dyed with madder on the same wool fibres, necessarily in a separate operation. This mixture can be analysed without difficulty. Pieces containing Ponceau 2R often also contain cochineal elsewhere, used with a freedom not found in earlier work; and in pieces that are probably later in date than these last, the cochineal is replaced by Amaranth (15). One rug contained an area dyed both with Amaranth and cochineal, and this did present a considerable problem, solved only by preparative thin-layer chromatography; however, it proves that Amaranth was considered a modern version of cochineal, just as Ponceau 2R was of madder. All this time, however, madder and indigo continue to be used in the same pieces. It is worth emphasising that these red azo-dyes cannot always be distinguished visually from their natural counterparts, even in good daylight; sometimes they can, when they have been used in excess to give an unnaturally brilliant shade, or when the colour (of Ponceau 2R; Amaranth is faster to washing) has bled on to the white warp or adjacent pile when too vigorously washed with modern detergents, while madder can be used to give sober brownish shades that are not duplicated by any one azo dye. Unfortunately, "chemical washing" in which the rug is treated with a mild bleaching agent, was sometimes used to degrade the azo-dyes, giving less saturated shades. This can often be detected by the difference in shade between the end and the root of each knot; in dye analysis it leads to various difficulties.

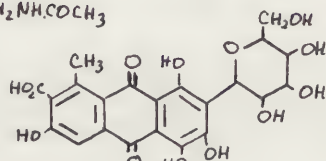
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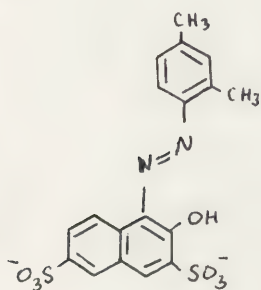
(10)



(11)

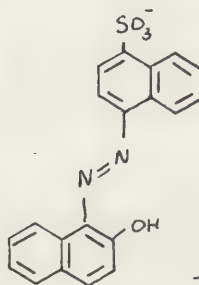


(12)



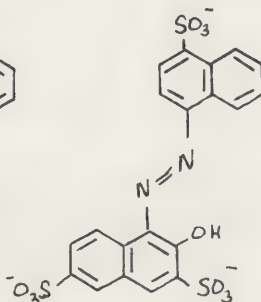
(13)

Ponceau 2R



(14)

Roccelline



(15)

Amaranth

The dye Roccelline (14), invented in 1878, was found in a Turkoman bag bought in Teheran in 1970. It was commonly used by Turkomans living in Persia, probably after 1925, and is especially prone to "bleed" in detergents.

With the dyes so far discussed we are on sure ground chemically and biologically, but are apt to draw only limited conclusions as to the provenance of a textile. Yellow dyes, on the other hand, are present in so many different plants that one has a much better chance of finding different plants used in different areas. The problems here are threefold; the compounds responsible for the colour, mostly flavones and flavonols, are much less easily distinguished from each other; they are less stable photochemically, so that many flavonol yellows fade to a cream shade, and are found to contain little of the original dye and much molecular debris; finally the two commonest compounds detected, quercetin and kaempferol (K,Q), are common to a vast number of different plants, so that one must try to identify minor, as well as major,

constituents. Thus, Sophora japonica ("Chinese yellow berries") is merely K + Q; Delphinium sulphureum ("isparuk") is K + Q + isorhamnetin; Rhamnus catharticus ("Persian berries") is K + Q + rhamnetin + rhamnazin. We are therefore developing techniques for purifying the flavonol dyestuffs by distribution between two-phase systems, buffers and organic solvents, using the known chemistry of these molecules, in order to separate the residual flavonols from the products of light-induced degradation. These components are still very similar to each other, and chromatographic methods are still needed to identify them; to be usable on a sufficiently small scale, very small chromatograms are run on commercial pre-coated plates, the solvent front typically moving some 2-3 cm. only (see Fig.2). Two different types of pre-coated plates (polyamide and partially acetylated cellulose) are used for each identification. A general, but preliminary conclusion is that Delphinium sulphuraeum, which is given names spelt isparuk, esperuk, asbarg, and other variants, but called "zelil" near Kirman, was in C19 the dominant dye of the nomadic peoples of Persia, the Caucasus, Turkestan, and (after export) much of India. This plant occurs widely in these areas, but is scarcely discussed in the literature of natural dyeing.

Weld (Reseda luteola) is a much superior yellow dye, and is found in classical urban Persian carpets of all the areas studied - but not in India or, so far, in Anatolia. Luteolin, the active principle, is a flavone, and is much more stable to light. Weld may have been traded over considerable distances, in much the same way as madder and indigo.

Some Indian carpets contain a yellow dyestuff quite distinct from these and not necessarily flavanoid. It was found both in a typical Moghul piece and in one bought new in 1883; only negative evidence is yet available as to its constitution, but all the most discussed dyes in the accessible literature have been ruled out. Again, further work on Indian carpets is clearly needed, if only to divide into reasonably homogeneous groups the products of that vast area. Only one group of Indian carpets, as judged by the dyes present, contains madder, and this would most naturally be attributed to Lahore, nearest to Persia; Ellore seems the most plausible area for pieces containing the strange yellow dye referred to above; while analysis of dyes implies the existence of a third group, which one would wish to assign to Agra. Whether such generalisations, tentatively made on the basis of a quite inadequate number of samples, would survive a serious investigation remains uncertain. We can, however, say that a number

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of specimens taken from carpets of the type traditionally described as "Herat" contain a set of dyes not distinguishable from those of typically Persian pieces often ascribed to Kirman; so that they are probably Persian, rather than Indian, in origin.

The work described was mainly carried out by Dr. Takeo Sugiura and Mr. Anthony Clemson, graduate students in Bristol; by Mrs. Soraya Rezakhani; and by a number of third-year undergraduate students: Patricia Broadbent, Robin Boycott, Christine Symons, Martin Lunnion, Nigel Woodland, Alex van der Heijden, Daryl Jeffrey, and Hugh Richards. The Science Research Council and the British Council provided funds, and a number of museums and private collectors provided specimens.

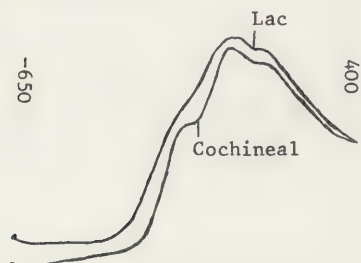


Fig.1. Spectra of lac and cochineal in pentan-3-one.

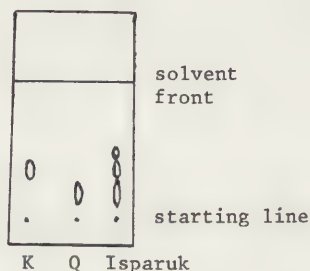
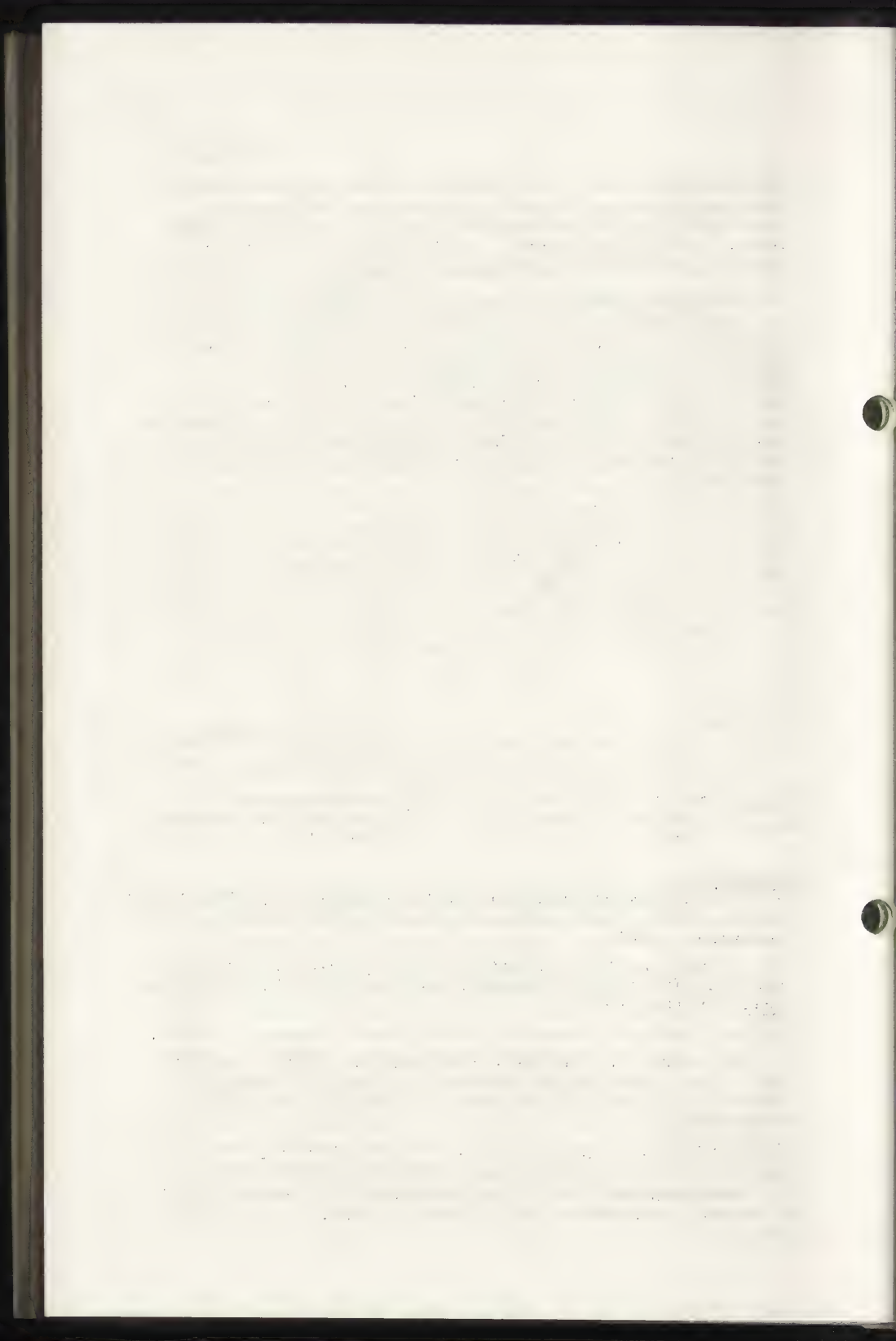


Fig.2. Chromatogram on Eastman K541V Polyamide (actual size)

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ANCIENT DYEING TECHNIQUES IN EASTERN
MEDITERRANEAN REGIONS

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

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ANCIENT DYEING TECHNIQUES IN EASTERN MEDITERRANEAN
REGIONS

L. Masschelein-Kleiner and L. Maes

SUMMARY

Dyer's craft is compared in three countries of Eastern Mediterranean : Nubia, Palestine and Egypt by analyzing textiles which are mostly dated between 0 and 600 AD. The metallic mordants are determined by X-ray fluorescence, the dyes by thin-layer chromatography, UV-V and IR spectroscopy.

Local plants seem to have been used in Nubia : a red dye is much like madder but with a higher content in purpurin, a bixin containing dyestuff is found in some yellow samples.

Tanins are more often found in Nubian and Hebrew textiles than in the Coptic ones and the same holds true for iron. Coptic textiles are characterized by the frequent presence of zinc, the use of luteolin for the yellow dyeings and by a beautiful red dye often mordanted with tin and which is much more like a cochineal than like Kermes.

INTRODUCTION

The present work is dealing with textiles from, Nubia (1) Palestine (2) and Egypt (3). Most of them are dated between 0-600 AD. Forbes (4) has collected a sound documentary material about dyeing technique from ancient texts. Meanwhile a good deal of dyer's recipes were kept secret and we often lack an accurate description of the plants or of the animals used to extract the dye. Chemical analysis may, therefore, play an useful part for the knowledge of this ancient technology. Analytical data concerning these regions were published very early by PFISTER (5,6,7,8,9) and more recently by ABRAHAMS and EDELSTEIN (10). The greatest care must be taken when interpreting the analytical results. It must be taken in mind that the same chemical compound often presents different natural sources. Further historical, botanical and zoological studies must then help to select between the hypotheses afforded by the analysis.

EXPERIMENTAL

ANALYSIS OF THE METALLIC MORDANTS

The analysis begins with the determination of metallic mordants by X-ray fluorescence because this method does not destroy the sample. The latest may then be used for further researches.

The threads, about 1 cm long are washed with demineralized water and a neutral detergent in order to eliminate metallic soils, mostly iron.

The metallic elements are determined by comparison with an undyed woolen thread and another one which was mordanted by a known metal. Tin, zinc, iron, copper and chromium are easily detected in this way. Aluminium requires a larger sample, at least 5 cm.

Experimental conditions

Kristalloflex 4 -Siemens SRS. Tube : Tungsten 40 kV-30 mA
Crystal : LiF. For aluminium determination : He-Flow. AdP crystal.

ANALYSIS OF THE DYESTUFFS

a) Extraction of the dyes

The dyes are extracted from the threads by boiling them in 0.5 ml HCl (diluted 1:1). After evaporation 0.5 ml water are added and boiled again. The dye is then extracted with amyl alcohol and the organic phase is washed twice

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with water in order to eliminate the sugars which are often associated with natural dyestuffs. Vat dyes such as indigo, purper (1,6-dibromoindigo) resist to this attack. They are characterized by the well-known reaction of reduction with hydrosulfite coupled with the reoxidation by air (5). Purper is confirmed by determining the presence of bromine with X-ray fluorescence. Some yellow dyes such as saffron or annatto belonging to the carotenoids group, are better extracted with petroleum ether instead of amyl alcohol.

b) Thin-layer chromatography

We found in 1967 (12-13) that the conditions proposed by WOLLENWEBER (11) for the analysis of synthetic anthraquinones also succeed in separating not only natural anthraquinones but also natural flavonoids (18).

Experimental conditions

Thin-layers : acetylated cellulose powder 10 % (Macherey, Nagel and Co- MN 300AC)..

Solvent : ethylacetate+tetrahydrofuran+water (5/35/47); detection reagent : 2-aminoethyldiphenylborate (Fluka AG, Buchs SG, Switzerland, nr 42810) : 1% in methanol. The plate must be watched under U.V.light (350 mμ).

c) Ultraviolet and visible spectroscopy (14)

This method requires only minute sample, It gives an effective help f.i. in differentiating weld from broom, in characterizing carminic acid, etc...

Experimental conditions

Spectrometer : Beckman DB ; solvents : methanol, amyl alcohol or petroleum ether (40°C-60°C)

c) Infrared spectroscopy (14)

The sample must be thoroughly free from sugars otherwise the intense absorption bands of the hydroxyl group, OH, will mask most other bands.

Experimental conditions

Spectrometer : Perkin-Elmer 221 ; KBr micropastille (diameter : 1mm) ; Condenser beam : 6 times. Compensation of the air absorptions with a 1m long gas cell.

RESULTS and DISCUSSION

Detailed description of the samples will be reserved to the catalogues in preparation by the individual museums to which belong the textiles (1,2,3). Indeed the analysis of the dyestuffs can contribute to a more accurate characterization of a museum piece. Our present purpose is somewhat different : it consists essentially in the com-

parison of the dyeing technology of three neighbouring people, Egyptians, Nubians and Hebrews.

NUBIAN TEXTILES

Metallic mordants

Aluminium seems of general use with all mordant dyes. Iron was found in a good half of the samples not only in brownish shades when tanins are present but also in red, yellow and green threads. On the contrary to the Egyptian and Hebrew textiles, the Nubian samples seldom contain zinc (4 among 147). The most amazing result is the presence of tin with certainty in a blue and a brown and as traces in four others (red, blue and brown). In Europe its use as mordant only dates from the 17th century on.

Red, orange and purple shades

Most Nubian red threads contain purpurin as the main constituent. Alizarin can only be detected in highly concentrated solutions. One explanation could be that the Nubian dyers used another plant than our European madder, *Rubia tinctorum*. Thanks to the Belgium National Botanic Gardens we had the opportunity to compare the composition in dyes of several kinds of *Rubia*. *Rubia munjista* and *cordifolia* both known under the name "munjeet" and *Rubia peregrina* contain much purpurin and very little or no alizarin. THOMPSON (15) reports on the other hand that another kind of plant, the so-called *Relbunium* species also contain much purpurin. They were used in Peru some 2000 years ago for dyeing textiles. Another explanation could be that the dyers knew a procedure to select purpurin in order to get a more carmine shade than with the complete madder (16). One carmine red sample contains another kind of dye very similar to a dyestuff we often found in Coptic textiles. This is likely to be an insect dye. More details will be given in the Egyptian textiles section.

Tyrian purple (1,6-dibromoindigo) was characterized in only one sample. It is produced by different kinds of molluscs such as *Murex trunculus*, *Murex brandaris* ... (17) and was no doubt the most highly-prized dye in the eastern Mediterranean countries (4). This fabric was likely imported to Nubia. Other purple shades were obtained by mixing indigo with the "Nubian madder" or with this latest dyestuff, gallotanin and iron.

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Yellow, beige, brown and green shades

Luteolin, the usual yellow dye we found in Europe (18, 19, 20, 21), was identified only in three yellow samples. We did, however, find it in most green shades mixed with indigo, and in olive shades where it was mordanted by iron. The UV-spectrum shows the presence of luteolin without genistein which tells in favour of weld (*Reseda luteola*) and not of broom (*Genista tinctoria*).

The other yellow threads are very difficult to identify. Thin-layer chromatography was found unsuccessful in analysing them either with our operating method or with those recommended by SCHWEPPE (22). They were dyed with something different than the commonest yellow dyestuff f.i. turmeric (*Curcuma longa*), saffron (*Crocus sativus*), Persian berries (*Rhamnus ifectorius*)... The HCl attack extracts a yellow solution but the sample remains yellow-colored. This fastness reminds us of the Palmyre yellow fabrics of which the color was attributed by PFISTER (5) to a natural wool tint. In the meantime, we tried to purify the extract in order to take a valuable infrared spectrum. Petroleum ether (40°C-60°C) separates a fraction showing some similarities with bixin, the principal component of annatto (otherwise called anatto, orlean, or rocou). This colouring matter is produced from the seeds of a small tree (*Bixa orellana*) and yields a bright orange color. FORBES reports it was known by the ancients although seldomly mentioned (4).

We are still looking for further data about this puzzling pigment.

A series of yellow, beige and brown threads were probably treated with tanins. Gallotanin compounds were found in about twenty samples not only in brownish shades but also mixed with yellow, blue and red dyes.

Blue shades

All the blue tones are achieved with indigo. They often contain traces of luteolin, purpurin and tanins.

HEBREW TEXTILES

Metallic mordants

Iron was found in half the samples, aluminium only in a good quarter just as zinc.

Red, orange and purple shades

Most red samples show the presence of the mixture alizarin and purpurin. On the contrary to Nubian textiles, alizarin is present in high concentration, which tells

in favour of *Rubia tinctorum*.

Here again, we found one carmine thread dyed very likely with the same insect dye we shall speak about in Coptic textiles and which was once recognized in Nubian fabrics too.

Tyrian purple was identified in one sample and it was mixed with indigo

Yellow, beige, brown and green shades

Here again like for Nubian textiles, we seldom found luteolin. Most yellow coloured samples show the same characteristics as the unknown yellow Nubian pigment. Bixin was identified with certainty in the infrared spectrum of a large sample.

The flax threads are mostly brown or beige. They contain tanins and iron. Catechin was found in two samples of NAHAL-HEVER, on cotton and on wool fibre. This compound is widely distributed in plants such as acacias and Mimosa trees which are two examples of trees among many others. Other tanins components and iron were present too.

Blue shades

They are all achieved with indigo.

EGYPTIAN TEXTILES

The results we describe here deal mainly with coptic textiles approximatively dated between Vth-VIIIth centuries. However a few samples were taken from earlier fabrics : those dated 0-IVth centuries show no special differences from coptic textiles with regard to dyes. A very old linen rose fabric (dated 3000 BC(25) seems to be very similar to the pieces from the Cairo Museum which were analyzed by Pfister (7). He said to have found saflor but this is very difficult to prove because carthamine the principal component of the dyestuff is very sensitive to most physical agents such as light and heat. In our sample we only found some gallotanin compounds.

Metallic mordants

Aluminium seems to have been used with the mordant dyes. Iron was found in about 20 % of the samples not only in brownish tints but also in red, yellow, green, purple coloured threads. Zinc appears with an unusual frequency : about 60 % and in some textiles all the threads contain this metal.

Here again as in Nubian textiles, we found tin in a series of red samples. This bears out the evidence that tin

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was used as a mordant at that time.

Red, orange and purple shades

Most red treads contain the mixture alizarin and purpurin which is to be found in madder, *Rubia tinctorum*. Meanwhile of the 40 which were examined about 10 tapestries do contain another red dye. They are all dated approximatively from the VIth-VIIth centuries, and most of them contain tin. Thin-layer chromatography separates five components among which a red spot with the same Rf as purpurin and another red one with the same Rf as carminic acid. The samples do not contain kermesic acid. This reminds us of an insect dyestuff described by Forbes (4). Besides Kermes from *Kermococcus vermilio*, Polish cochineal from *Margaredes polonicus* and ficus from *Coccus lacca* he reports that "a real cochineal from an insect similar to *Coccus cacti* was known in the Ararat valley". "In later Jewish documents, it is said that the *Cactus Cochenillefera* was grown near Nablus and that the insect producing the dye was fed on it..."

The unknown red dye could be this kind of cochineal but of course we should have to find this insect in order to confirm or not this hypothesis.

All the purple shades we analyzed were achieved by mixing madder and indigo.

Yellow, beige brown and green shades

All the coptic yellow samples are dyed with luteolin, likely from *Reseda luteola*. Brown shades are often achieved with madder on iron, tanins were rarely found. Green threads are obtained with indigo and luteolin.

Blue shades

They are all achieved with indigo.

CONCLUSIONS

In surveying the dyer's craft of the three people, Nubians, Hebrews and Egyptians, it appears that about the same methods were used all over the three countries. Dyeing with mordant dyes and with vat dyes was known of since early times.

Nubian dyers seem to have exploited local plants for the red and the yellow shades. They used a plant similar to madder for the red dyeings but with a higher content in purpurin.

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A dyestuff containing bixin like anatto was found in some Nubian yellow samples but there is nothing to prevent that natural coloured wool was used too. On the contrary most Coptic yellow threads are dyed with luteolin, likely from *Reseda luteola*.

A beautiful carmine is to be pointed out in Coptic tapestries and in some Nubian and Hebrew textiles. This amazing dye is more often found with tin, a mordant which was rediscovered in Europe only in the XVIIIth century ! Because of the presence of carminic acid without kermesic acid, this dye seems to be much more like cochineal than like kermes. It could be the *Coccus* insect Forbes reported to have been feeding near Nablus.

Tanning are more frequently identified on Nubian and Hebrew textiles than is Coptic ones, the same holds true for iron. Zinc is present in a good deal of the Coptic samples and most seldomly in Nubian ones.

Tyrian purple was found only twice in all the pieces we analyzed. No wonder : this famous dye was also the most highly-prized.

The present study brings out the high level of perfection the dyers of the Eastern Mediterranean countries had reached. This bears witness to the cleverness of man since early times.

ACKNOWLEDGEMENTS

I wish to express my gratitude to The Oriental Institute of the University of Chicago, to The Art Institute of Chicago and to Mrs C.C.M. Thurman, to The Peabody Museum of Archaeology, to Ms J.S. Brandford, and to Mr L.V. Zabcar, to Professor Gichon and the Unit of Roman Frontier Studies of Tel-Aviv University and to Mrs Dosogne and the "Musées Royaux d'Art et d'Histoire" in Brussels for purveyance of precious samples and for giving us the opportunity to carry out this study. I am most grateful to Mr. A. Lawalrée from the "Jardin Botanique National de Belgique" who gave me several identified plants. To Mrs M.C. Peeters-Keyaerts is acknowledged for her helpful assistance.

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- (2) Hebrew textiles : the textiles were excavated by The Unit of Roman Frontier Studies of Tel-Aviv University, Professor M. Gichon, in the Dead Sea region. They are dating between 100 BC and 300 AD. Three samples which were found in a cave in Nahal-Hever are supposed to be either Arabic or from the Middle Ages.
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THE ANALYSIS OF FLAVONOIDS IN NATURAL
YELLOW DYESTUFFS OCCURRING IN ANCIENT
TEXTILES

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5th Triennial Meeting
Zagreb, 1978

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Abstract

It appeared from literature that the most occurring yellow dyestuffs in ancient textiles contain flavonoids.

A research programm for the separation of flavonoids was executed by means of thin-layer chromatography. This research resulted in method of analysis, with the help of which some hundreds of well-dated textile samples of the period 1500-1850 have been investigated.

From literature research it was expected that the analysis of yellow dyestuffs would give further clues for the establishing of the date of the textile object investigated.

It appeared, however, from the research that about 80% of all samples was dyed with Weld and that no further clues about the date can be expected by analysing yellow dyestuffs in ancient textiles.

1. Introduction

The yellow dyestuffs used in the textile dyeworks until the invention of the synthetic dyestuffs (ca. 1860) were all of vegetable origin.

The most important yellow dyestuffs, named in literature and dyer's manuscripts, are the following:

Weld (*Reseda luteola* L.), Dyer's Broom (*Genista tinctoria* L.), Persian Berries (*Rhamnus amygdinus*, *R. oleoides*, *R. saxatilis*, *R. alaternus*, *R. infectorius* L., *R. cathartica* L.), Fustic (*Morus tinctoria* L.), Young Fustic (*Rhus cotinus* L.), Quercitron (*Quercus tinctoria* L.), Safflower (*Carthamus tinctorius* L.), Saffron (*Crocus sativus* L.), Turmeric (*Curcuma longa* L.), Orlean (*Bixa orellana* L.), Pomegranate (*Punica granatum* L.), Sumach (*Rhus coriaria* L.), Cutch (*Acacia catechu* Willd.) and other tannin containing plants.

Several of these plants are already mentioned in remote ages. It is Pliny who, in his "Historia Naturalis", mentions the yellow dye "Lutum", which stands for Weld. The dyes used in the ancient world and mentioned by Forbes (6) and Singer (7) are o.a. Weld, Dyer's Broom, Persian berries, Saffron, Safflower, Orlean, Turmeric, Pomegranate and Sumach.

There exists a number of early German manuscripts of the 14th century, among which the "Oberdeutsches Farbebüchlein" (8) in which a.o. Weld, Berberis and several *Rhamnus* arts are mentioned. Weld is also mentioned in Flemish dyers guild rules in the period between the 12th and 15th century.

One of the first dye-books, written in the Dutch language, "T Bouck vā wondre" (9) of 1513, mentions Weld exclusively.

"Plictho de Larte de tentori" (10), an Italian dyer's manuscript of 1548 mentions the following dyes: Weld, Dyer's Broom, Young Fustic, Safflower, Fenugreek, Turmeric, *Rhamnus cathartica* and Pomegranate.

It is after the discovery of America that also Fustic is more often

found in dye-recipes, though sporadically.

There is a wider scale of yellow dyes available in the 17th century. Yet, it is mainly Weld, Dyer's Broom, Fustic and also Turmeric that are mentioned in manuscripts of that period(11).

It is the frenchman Colbert who introduces the distinction between the "grand(bon) teint" and the "petit teint".

Weld belongs to the "Grand teint", Young fustic to the "Petit teint".

The directions of Colbert have been translated in other languages many times. Haak(12) mentions the use of Weld, Turmeric, Fustic and Dyer's Broom in 1733.

The period between 1750 and 1850 is a period of great inventions and also of frequent experimenting in the field of textile dyeing.

Important treatises were written by Hellot in 1730 (13), Berthollet in 1791 (14) and Bancroft in 1794 (15).

These books have also been translated many times and it is the Dutchman Boot (16) who, in 1820, states Fustic, Quercitron, Weld, Yellow berries Orlean and Young fustic as the most important yellow dyestuffs.

He also indicates that the best results(at that time)are achieved with Quercitron. This dyestuff was introduced in England by Bancroft(15) in 1794 and occupies after that time a significant position there.

Research on Dutch and Flemish tapestries of the 16th and 18th century learned that in that period Weld was the most important yellow dyestuff. Also Dyer's Broom and Fustic were found, but less frequent(18,19).

We may divide dyes according to:

1. Dyeing method

2. Chemical constitution

It is possible, when dealing with the dyeing method, to distinct the natural dyes in three categories, namely direct dyes, mordant dyes and vat dyes. Nature knows only two vat dyes, namely Indigo and Imperial Purple, respectively blue and violet, which brings us to the conclusion that yellow dyes are only found with direct and mordant dyes.

With direct dyes is meant, dyes that directly, without any further auxiliary can be used for dyeing textile fibres. That is why most of these dyes are fit for use both on cellulose and protein fibres.

The use of mordant dyes, however, is preceded by a treatment of the fibres with a metal salt and then the textile material is dyed with an extract of the dyeplants, as a result of which an insoluble metal complex precipitates on the fibre. The colour obtained depends on the metal salt used. This method is in most cases only possible on protein fibres.

Nearly all yellow dyestuffs are mordant dyes and the most important and most occurring yellow dyes, namely Weld, Fustic, Persian berries, Dyer's Broom, Young fustic and Quercitron are mordant dyes and belong chemically to the Flavonoids.

We limited therefore, in the beginning, our research to the analysis of Flavonoids.

2. Chromatographical research

2.1 Experimental

After some first experiments in the field of yellow dyestuffs in ancient textiles had been carried out(17), the research was restricted during the last years to mainly the analysis of red dyestuffs.

Because of the fact that these analyses ended in good results(22)

and that those with yellow dyestuffs have not completely been satisfying, attempts were made to develop a good analysis method for this group of dyestuffs.

We limited our research in the beginning to the Flavonoids, as already stated in the Introduction. Experiments were also executed with other occurring dyestuffs, but the results of them are still to be completed. Much literature is written on the separation of Flavonoids by means of thin-layer chromatography(1).

These well-known data, namely combinations of adsorbents and eluents, were therefore taken as starting-point. They were also used for the starting of experiments concerning the choice of adsorbents, polarity of elution and means for detection.

2.2 Adsorbents

1. Pre-coated TLC Plates Silica gel 60 (Merck)
2. Pre-coated sheets Polygram Cel 300 AC-10 (Macherey & Nagel & Co)
3. Pre-coated sheets Polygram Cel 300 AC-30 (" ")
4. Pre-coated sheets Polygram Cel 300 ECTEOLA (" ")
5. Pre-coated sheets Polygram Cel 300 DEAE (" ")
6. Pre-coated sheets Polygram Cel 300 CM (" ")
7. Pre-coated sheets Polygram Cel 300 PEI (" ")
8. Pre-coated sheets Polygram Cel 300 PEI/UV₂₅₄ (" ")
9. Pre-coated sheets Polygram-Polyamid 6 (" ")
10. Pre-coated plates Nano-Plates SIL-20 (" ")

2.3 Eluents

- A. Toluol/ethyl formiate/formic acid/5:4:1/ (3,4)
- B. Tetrahydrofurane/ethyl acetate/water/35:6:45/ (2,5)
- C. Chloroform/methanol/15:1/ (1)
- D. Chloroform/ethanol/3:1/ (1,3)
- E. Chloroform/ethanol/ 1:1 / (1)
- F. Ethyl acetate/methyl ethyl ketone/formic acid/water/5:3:1:1/(1,2,4)
- G. Petroleum ether/ethyl acetate/1:3/ (1)
- H. Petroleum ether/ethyl acetate/1:1/ (1)
- I. Chloroform/ethyl acetate/methyl ethyl ketone/formic acid/
water/methanol/15:5:1:1:6/
- J. n-Butanol/acetic acid/water/6:1:2/ (1)
- K. Methanol/acetic acid/water/90:5:5/ (1)
- L. Chloroform/methanol/methyl ethyl ketone/12:2:1/ (1)
- M. Methanol (1,3)
- N. Methanol/water/4:1/ (1,3)
- O. Acetone/water/1:1 / (1)
- P. 2-Propanol/water/3:2/ (1)
- Q. Petroleum ether/ethyl acetate/methyl ethyl ketone/formic acid/
water/1:8:3:1:1/
- R. Chloroform/ethyl acetate/methyl ethyl ketone/formic acid/15:5:3:1/
- S. Chloroform/ethyl acetate/methyl ethyl ketone/methanol/15:5:3:5/
- T. Chloroform/ethyl acetate/methyl ethyl ketone/methanol/15:5:3:1/
- U. Chloroform/ethyl acetate/methyl ethyl ketone/formic acid/
30:10:6:1/
- V. Chloroform/ethyl acetate/methyl ethyl ketone/methanol/formic
acid/15:5:3:6:1/

- W. Chloroform/ethyl acetate/methyl ethyl ketone/methanol/formic acid/water/15:5:3:20:1:1/
 X. Chloroform/ethyl acetate/methyl ethyl ketone/formic acid/30:5:6:1/
 Y. Chloroform/ethyl acetate/methyl ethyl ketone/formic acid/30:5:3:1/
 Z. Chloroform/ethyl acetate/methyl ethyl ketone/formic acid/60:5:3:1/

2.4 Detection

- I .1% solution of "Naturstoffreagents"(2-aminoethyl diphenylborate) in methyl alcohol
- II .Ultraviolet light with a wavelength of 350 nm
- III .Ninhydrin
- IV .Vapour of ammonia
- V .Bromocresol green
- VI .Phosphomolybdic acid
- VII .0.5 normal solution of KOH
- VIII .1,3-Dihydroxynaphthalene(naphtho-resorcinol)-trichloroacetic acid
- IX .Antimony pentachloride
- X .Dichromate-sulphuric acid
- XI .2,6-Dibromoquinonechlorimide
- XII .Ferri chloride

2.5 Colouring matters

Weld(1',2'), Dyer's Broom (1',3'), Fustic (4',5'), Quercitron bark (10',11'), Young fustic(12'), Sumacberries(12')(World wide Herb Distributors, Montreal), Bacca Rhamni Persien, Baccae Rhamni infectoriae Erlangenses (6',7',8',9')(Courtesy Doerner Institute, Munich), Apigenin (2'), Maclurin(5'), Kaempferol(9'), Emodin(8'), Quercitrin(10')(Fluka), Luteolin(1'), Fisetin(12'), Rhamnetin(6'), (Roth), Morin(4'), Quercetin(11')(Merck), Genistein(3')(ICN)
 Dyed wool: Pure wool was mordanted with Alum and accordingly dyed with dyestuff extracts of Weld, Dyer's Broom, Fustic chips, Quercitron bark, Young fustic, Sumac berries and Persian berries.

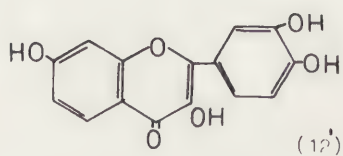
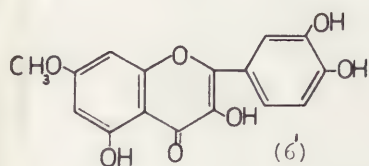
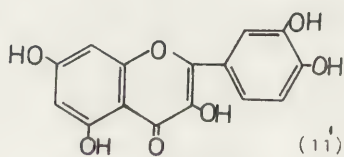
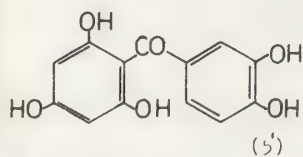
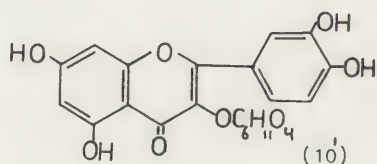
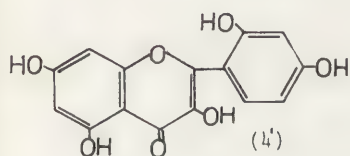
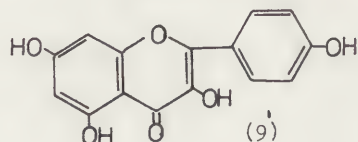
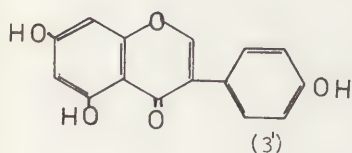
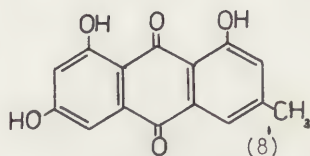
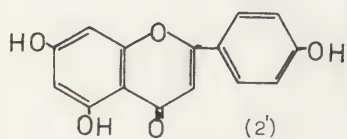
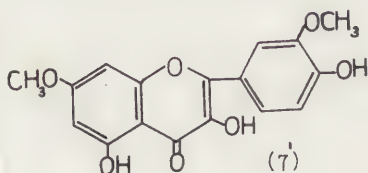
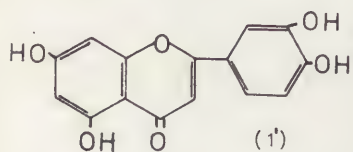
2.6 Procedure

About 0.5 mg of each colouring matter is dissolved in ca. 0.5 ml methyl alcohol. The natural dyestuffs are, if heterosides are present, first hydrolyzed with boiling 10% hydrochloric acid and then dissolved in methyl alcohol. The dyed wool is boiled with 10% hydrochloric acid in order to decompose the metal complex. Then the dyestuff is dissolved in methyl alcohol. The methyl alcohol solution is applied to the plate by means of a Pasteur pipette with a point-diameter of about 0.3 mm.

The results of the experiments are incorporated in the Tables I, II.

2.7 Conclusion

It appeared from the experiments that good separation of the mentioned dyestuffs can be achieved by the use of the following combinations.



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Table I

A etc. = eluent	1, 2, 3, 10 = Adsorbent															
	-- = very bad	- = bad	o = moderate	+	= good	++ = very good										
	1 A	10 A	2 B	3 B	1 C	1 D	1 E	1 F	1 G	1 H	1 I	10 I	1 Q	1 R	10 R	1 S
Fistic	-/+	+	o/+	-/o	-/o	-	-	o/+	-	-/o	o/+	o/+	o	+/++	++	o
Corin	o	+	o/+	o/+	-	-	--	o	o	o	o	+	o	++	++	-
Maclarin	-/o		o/+	o										++	++	
Persian berries	o/+	o/+	-/o	-/o	-	-/-	--	-	-/-	-	o	o/+	-/o	o/+	+/++	-
Kaempferol	-/o	o	o/+	o/+	-	-	-	o	-	o	o	o/+	o	o/+	++	-
Rhamnetin	o	+	--	o/+	o	o	-	o	-	o	o	+	--	o/+	++	o/+
Erodin	+/++		o/+	o/+										++	++	
Quercitron x	-/o	o	--	--	-	-	--	--	--	-	-	o	--	o/+	+	o/+
Quercitrin	o/+	-/o		o/+	-	-	--	-	--	-	-	o	--	o/+	+	o
Quercetin		o	--	-					--	-	o	o/+	-	o/+	+	o/+
Fisetin	o	o	o	o/+					o	+	o	--	-	o/+	+	o/+
Dyer's broom x	-	-	-	-	-	-	+/++	+	-	-	+	++	+	-	o	-
Weld	-	o	-	-	-	-	-	o	-	-	-	o	-	o	+	-
Sumach berries															o	
Luteolin	-	o	-	-	-	-	-	o	-	-	-	o	-	o	+	-
Apigenin	-	o	-	-	-	-	-	o	-	-	-	o	-	o	+	-
Genistein														o	+	

x Quercitron bark and Dyer's broom (World wide Herb Dist.) do not show the spot-pattern of the expected pure components.

Adsorbent no.1 Pre-coated TLC plates Silica gel 60

Adsorbent no.10 Pre-coated plates Nano-Plates Sil 20

Note: We choose, in the course of the continued research on yellow dyestuffs, to working with Nano-plates Sil 20. The development of High Performance Liquid Chromatography (HPLC) led to a renewed research in the field of Thin-Layer Chromatography (TLC). New methods were developed to make it possible to produce very small particles of silica with detailed described por-diameter and size. These silica particles were first used in the HPLC-columns and later also applied on plates. The binding medium of the layer was improved much and resulted in the production of the abovementioned Nano-plates.

Advantages of these plates are their separation capacity, which is greater than that of the traditional silica plates, and their detection limit which lies in the nano-range. These advantages are important for the analysis of dyestuffs in objects of art, in respect to the sample-size, which should always kept within strict limits.

Eluent R Chloroform/ethyl acetate/methyl ethyl ketone/formic acid/15:5:3:1/

Detection of the spots I: 1% "Naturstoffreagens A" in methyl alkohol
 II: Ultraviolet light wavelength 350 nm
 XII: After I and II spray with a solution of 5% Ferri chloride in methyl alkohol.

The results are shown in Figure 1

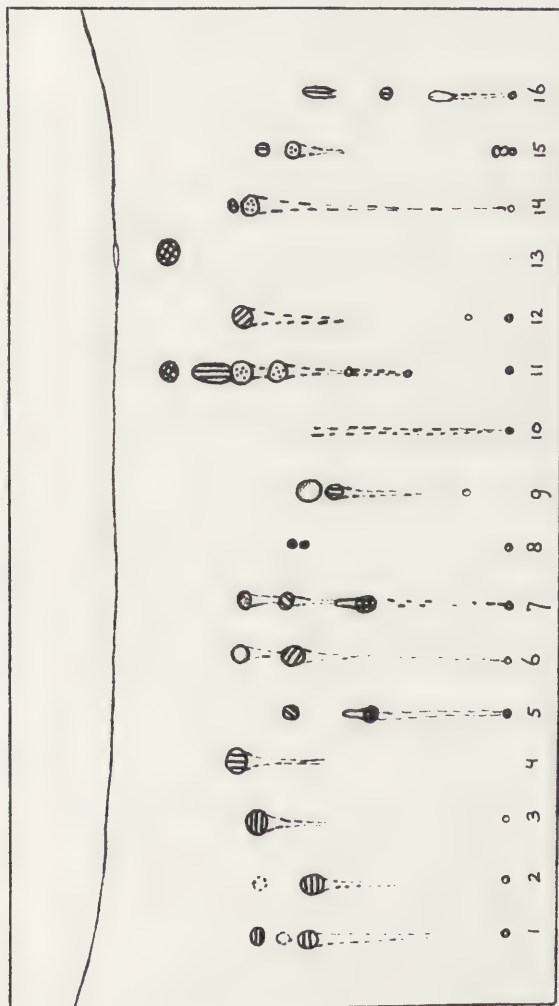
3. Analysis of yellow (flavonoids) dyestuffs in textile materials of the period 1500-1850.

3.1 Introduction

The research on red dyestuffs of the period 1450-1600 (22) completed, it was suggested that it might be useful to investigate also the occurrence of yellow dyestuffs in a certain period. We chose for the period 1500-1850, because a great number of changes could be expected in that period. There is, e.g. in this period the import of Fustic from America, there is also within this period, the period that knew many experiments and inventions and began around 1750. The invention of the first synthetic dyestuff took place around 1860. We asked, because of this, a great many museums for well-dated samples of the period 1500-1850, a request to which many of the museums reacted positively. The samples were taken by the owners and curators of the collections concerned. The authors of this article are most grateful for the co-operation they experienced when gathering samples for their research, co-operation without which research could not have been effected.

Schweizerische Landesmuseum, Zürich, Bayerisches Nationalmuseum, Munich, Victoria & Albert Museum, London, Kostuummuseum, 's Gravenhage, Muzeum Narodowe, Poznam, Museum of Decorative Art, Copenhagen, Ministerio Da Educacao Nacional, Instituto de José de Figueiredo, Lisbon, Gewerbe Museum, Basel, North Western Museum & Art Gallery Service, Manchester, Museum of Fine Arts, Boston, Kunstindustrimuseum,

Fig. 1



⊖	pinkish yellow	⊖	orange/brown
⊖	whitish	⊖	pink
⊖	blue	⊖	yellow
⊖	yellow/green	⊖	orange

1. Weld
2. Luteolin
3. Apigenin
4. Genistein
5. Fustic
6. Morin
7. Maclurin
8. Young Fustic
9. Fisetin
10. Persian berries
(*Rhamnus catartica*)
11. Rhamnetin
12. Kaempferol
13. Emodin
14. Persian berries
(*Rhamnus infectorius*)
15. Quercitrin
16. Sumach berries

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Oslo, Staatliche Museen Preussischer Kulturbesitz, Kunstgewerbe museum, Berlin, Gewebesammlung, Krefeld, The Metropolitan Museum of Art, New York, The Cleveland Museum of Art, Cleveland, Kungl. Livrustkammaren, Stockholm, Alfredo Clignon, Restauratore Arazzi e Stoffe, Firenze, The Textile Conservation Center Inc.

3.2 Sampling

We received hundreds of samples (c. 500), however, which were not equally spread over the several periods demanded for. And all samples, a few exceptions taken apart, came from Europe. Table III gives the origin and period of the samples analysed so far.

Table III

Origin	date and number of samples				
	before 1500	1500- 1600	1600- 1700	1700- 1800	after 1800
Italy	3	20	20	14	5
Spain	1	6	5	3	1
France	-	5	10	62	1
Germany	-	2	3	5	3
Netherlands	-	16	6	20	6
Portugal	-	-	7	2	4
Scandinavia	-	4	11	12	5
England	-	1	10	6	4
U.S.A	-	-	-	1	-
Switzerland	2	5	13	10	1
Oriental	-	1	2	2	1

The analytical system, mentioned in the conclusion (2.7) was used for dyestuff analyses of the abovementioned samples.

3.3 Discussion and Results

The results of the analyses are set down in Table IV and Figure 2. This table shows that about 80% of the samples was dyed with Weld, which corresponds with the results of previous research on a group of Northern Dutch tablecloth(18).

Though the analytical system offers good results on pure colouring matters and on new wool, dyed with natural dyestuffs, analyses of ancient textile material still confront us with problems.

There is the fact that 20% of the analysed samples is still classified as unknown. One might conclude that these dyestuffs do not belong to the group of Flavonoids, which, however, is not the case. The presence of Luteolin was often established. Not, however, the, to Weld belonging, Apigenin. This lacking of Apigenin might find its cause in several reasons:

a) A type of Weld is used that contains Luteolin exclusively.

b) It is known that many Flavonoids are not stable photochemically and fade easily to an almost whitish shade. The main component in Weld is Luteolin, Apigenin is present in lesser quantity. This small quantity could have been disintegrated entirely.

Another aspect is the difference between Weld and Dyer's Broom. They contain Luteolin and Apigenin and Luteolin and Genistein respectively. There is only a slight difference between the Rf-value of Apigenin and Genistein, which is not a problem with pure colouring matters. With ancient textiles, however, misinterpretation is not unthinkable because of the impurities present, which might change the Rf-value.

We could not confirm the presence of Fustic and Quercitron, though it could have been expected, according to dyer's manuscripts.

3.4 Conclusion

It appears, from the preceding research, that analysis of yellow dyestuffs does not offer any further information about the dating of the textile object of art under investigation.

Acknowledgement

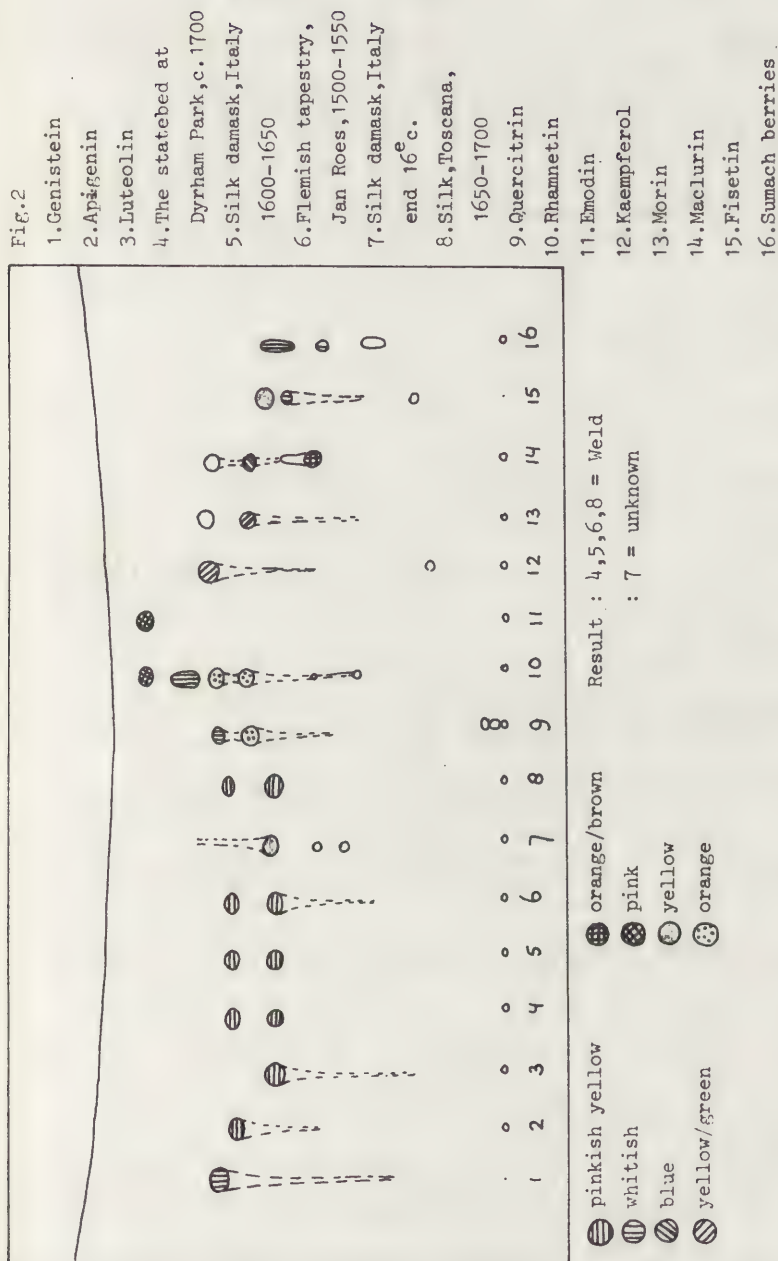
The authors are grateful for the co-operation of the already mentioned museums in obtaining the samples.

The practical chromatographic research could not have been realised without the help of Miss C.M. Horn. Her patience and accuracy formed an important contribution to our research. Also the assistance of Miss E. van Boekel was much appreciated.

TABLE IV Results of the dyestuff analyses.

Origin	Dyestuff	before 1500	1500-1600	1600-1700	1700-1800	after 1800
Italy	Weld	3	12	15	11	5
	Unknown	-	8	5	3	-
Spain	Weld	1	5	3	3	1
	Unknown	-	1	2	-	-
France	Weld	-	4	10	60	1
	Unknown	-	1	-	2	2
Germany	Weld	-	2	2	5	1
	Unknown	-	-	1	-	-
Netherlands	Weld	-	15	6	20	4
	Unknown	-	1	-	-	2
Portugal	Weld	-	-	2	2	4
	Unknown	-	-	5	-	-
Scandinavia	Weld	-	4	9	9	4
	Unknown	-	-	2	3	1
England	Weld	-	1	10	6	1
	Unknown	-	-	-	-	3
U.S.A.	Weld	-	-	-	1	-
	Unknown	-	-	-	-	-
Switzerland	Weld	2	5	12	10	-
	Unknown	-	-	-	-	1
Oriental	Weld	-	1	-	-	-
	Unknown	-	1	1	2	1

Fig. 2



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SOME COMMENTS ON THE EVOLUTION OF
COMPLEX WEAVE STRUCTURES FOUND IN EARLY
PATTERNED SILKS

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Zagreb, 1978

SOME COMMENTS ON THE EVOLUTION OF COMPLEX WEAVE
STRUCTURES FOUND IN EARLY PATTERNED SILKS

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The purpose of this paper is to show the early appearance of compound weaves in patterned silks, firstly in China and later in Near East, and to briefly point out the fibre and weave characteristics which can be detected through technical analyses. While our type of examination has allowed us, primarily through technical study, to see the internal constructions of textiles and to assess their various degrees of complexity, these technical finds in turn must be coordinated with valid historical and archaeological associations. Thus those specimens which can be reliably dated serve as references for more correctly identifying those which are devoid of any direct evidence of date or provenance. An attempt is also being made in our joint teamwork to identify a time sequence in the development of weave structures and to relate them to the type of loom equipment which may have been used.

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During late antiquity and the early middle ages, medieval society and culture which had evolved from a common Graeco-Roman background, had their centres and urban settlements situated in the Meditterreanean. Amongst the large quantity of textile remains from this Meditterreanean culture, a number of which are preserved in European Church treasures and international Museums, it is the exquisitely patterned fabrics which exemplify the level of artistic and technical skill, and which unfailingly enliven our imagination.

It has been obvious to textile experts that patterned textiles woven in silk fibre constitute the more significant finds, for since quite early antiquity silk has been the more sought-after medium, not only for the making of exclusive garments and costumes, but also for ritualistic purpose. That in the past silk was woven not only for temporal use but also to adorn and protect the dead for his maintenance in after-life, is attested by excavations in diverse sites where important burials have been unearthed. Repeatedly one has encountered that silk fabrics in intricate weaves and patterns - combined results of amazing technical skill, artistic concept and perseverance in production - have been used as an essential homage to the dead and his life thereafter.

In order to understand the preponderant role played by the silk fibre as a medium for woven textiles, one has to revert to altogether another sphere than the Meditterreanean, to the country where the silk fibre was presumably discovered and its weaving undoubtedly developed, that is, China of the Han Dynasty (206 B.C. - 220 A.D.). In Han China, during such ancient times, silk was already being woven with incredible skill and virtuosity. As far as actual specimens are concerned, although destroyed by natural elements and other factors, a substantial amount of silk fragments from this ancient past have survived

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the vicissitudes of time and therefore serve as direct evidence of both the art form and weaving technology which prevailed at the time. Moreover, the conditions of find of the Han Dynasty patterned silks have been well recorded and described by the well-known explorers, a fact which greatly helps in the matter of reliably attributing the fabrics within this given period. Amongst the most notable finds are those made in 1913-1916 by Sir Aurel Stein, in the site of Lou-lan in Eastern Turkestan, and again the fragments discovered in 1925 by P.K. Kozlov at the nomadic site of Noin-Ula in northern Mongolia. More recently, since 1959, the excavations carried out in mainland China have brought to our attention an impressive quantity of silk fabrics from the Han Dynasty, amongst which some have woven pattern. Significant Chinese finds have been made in 1959 in Niya (Minfeng) in the Uighur Autonomous Republic (Sinkiang), and in 1972 at Mawangdui in Chang-sha, Hunan province. In the latter site the excavation of an intact burial has been dated circa 160 B.C.; the noblewoman at the time of burial was adorned with many layers of robes and textiles. Sir Aurel Stein's finds are preserved in the National Museum in New Delhi and also the British Museum; P.K. Kozlov's finds are kept at the Hermitage Museum in Leningrad. It will be remembered that some very important finds of early Chinese textiles were made by the Hedin Expedition, and Vivi Sylwan's detailed publications on these finds serve as an important background for a preliminary understanding of the textile material of this period.

It may be mentioned that as recently as ten years ago, it had seemed quite difficult to break new ground in the study of these early Chinese patterned silks. While several textile experts, starting from 1920, had provided reports on the recurring technical and iconographic characteristics to be found on the Han patterned silks, only a limited few had the opportunity of studying the specimens at first-hand and to understand their internal structure. Since 1966, a joint project and team-work has enabled us to make direct and repeated studies of some of the important specimens. While I was able to make several trips to study the specimens at first-hand at the National

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Museum and the Hermitage, Mr. G. Vial, Technical Secretary at C.I.E.T.A., was provided with magnified photographs with scale showing the weave structure, and also with samples of several Han and T'ang Dynasty (618 - 907 A.D.) specimens. These samples were accorded by the authorities in the interest of scientific research. This work of meticulous technical observation on various silks, including the ones from Tun-huang, has therefore been in progress since 1966. Detailed technical analyses of weave are carried out by Vial; together with the co-ordination of historical and archaeological associations made by the eminent specialist E. Lubo-Lesnichenko and by myself the technical analyses have been published in different journals since some years. A corpus of our work on various samples, including microanalyses of the fibre, carried out by Mme H. Meyer, fibre specialist, dye analyses by Mme Hofenk de Graaf, dye specialist as well as other technical results offered by the National Museum Laboratory in New Delhi, is actually under preparation.

Our joint study has so far shown us that even in regard to the nature of ancient silk fibre many problems continue to persist. While high-powered microscopes (we have been able to obtain images of a few specimens taken with the Electronic Scanning Microscope) show extraordinarily aggrandized image of the section under examination we cannot be certain that the peculiar characteristics exist uniformly on another section of the same fibre. We have not been able to test such features such as the μ or mean diameter of the silk thread; we have been unable to count the number of brins per thread, to test the "circularity coefficient" and "lousiness" which have been done by specialists such as Dr. Junro Numone from Japan. Our inability has been due to the fact that the samples we have are from historical textiles, and the minimum amounts have been taken for tests (in our publications we always mention the exact provenance and the dimension of the sample under discussion). These samples have sometimes to be washed because of dirt deposit; they are extremely brittle due to age and due to conditions of preservation; in other words, they are excessively difficult to handle because of their extreme fragility. We have not examined the mean diameter of

the silk yarn for 1) the length of the yarn which we have at our disposal is understandably very short, and brittle, and 2) specialists like F. Guicherd had pointed out, in a silk thread which is reeled off the cocoon, attaining a length of 800-1000 meters, it is extremely difficult to find a diameter which remains uniform throughout. According to Guicherd, the diameter of a bave varies according to the quality of the cocoon, and variations exist between one cocoon and another. In fact, variations of diameter exist even within the same cocoon; the maximum diameter is usually located in the central layers of a cocoon (see F. Guicherd, Cours de Théorie de Tissage, Editions Sève, Lyon 1946, pp. 11-17). We do not believe that the limited samples which we have at our disposal will allow us to pronounce, like some other specialists, on the provenance of the cocoons themselves, as to whether the cocoons were reared in Han China, modern China, Syria, Japan or Central Asia (see R. Pfister, Textiles de Palmyre, Vol. I, Paris 1934, pp. 39, 55-58).

We have therefore laid our primary emphasis on the analyses of the weave construction. An essential aspect of the weave analysis is to reconstruct and to render clearly visible through diagrams, the action of the warp ends and the function of the weft picks - in other words each and every peculiarity of the system of interlacing. Among the important elements are the *découpeure*, repetition of the pattern units, and the measurement of each repeat. Such analyses, where the minutest occurrences and peculiarities are recorded with exactitude and precision, have helped to restore a balance between widely speculative theories regarding the external features of the fabric on the one hand, and the internal structure on the other. It is our estimation that through our comparative studies carried out in the Museums directly on the specimens, and whenever it has been possible, together with samples put to appropriate chemical and technical tests (ably supported by micro and macrophotos) new characteristics which had previously remained unperceived have now been detected.

The weave structure which is almost without exception employed in the patterned silks from the Han period is referred to as "warp-faced compound tabby". In the C.I.E.T.A. vocabulary the warp-faced compound weaves are defined as having a warp divided into series normally of different colours, and one weft that serves two functions. Ends selected from any series form the pattern on the face of the

cloth, while all other ends appear only on the reverse. Even picks of weft interlace with warp either in tabby (or twill), and uneven picks lie between the ends on the face and those on the reverse holding them apart, and automatically lengthening the floats so that a pattern results (see Harold Burnham, "Technical Aspects of the Warp-faced Compound Tabbies of the Han Dynasty", Bulletin de Liaison C.I.E.T.A., N° 22, Lyon 1965). All the polychrome patterned silks from the Han Dynasty that have been found, as well as the earlier one from Pazyryk, dating from 5th - 3rd century B.C., are in this construction; the binding in the polychrome finds are invariably in tabby, whereas in the monochrome patterned silk, while the ground is in tabby, the décor is occasionally effected by 3:1 twill.

It now appears to us that the technique of the "warp-faced compound tabby" was executed on a type of equipment analogous to the "pattern-rod" loom. Although the "pattern-rod" loom in itself suggests an apparatus of a simple type, yet such a weaving technique presupposes intricate and laborious manipulation, more markedly so in the instances of large horizontal repeats, where variations within each pattern-unit imply that each section had been independently prepared and executed, without any mechanically controlled relation to each other. The summum of skill should be attributed to those master engineers who co-ordinated the elaborate sequence of colour and design with the task of "setting-up" of the warp.

It has already been pointed out that even meticulous textile specialists have on occasions failed to make a clear distinction between weaving "effects" and weaving "techniques". This assessment is important, for it involves an essential distinction which must be made between the actual weave-structure and its visual aspect. In advanced technical analyses the detection of an "irregularity" or a "fault" in weave can be quite significant and can in itself become a revealing factor regarding the nature and peculiarities of either the loom device or of the weaving process.

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The standard width of all silks during the Han period was 50'38 cm. This fact has been corroborated both by ancient texts and the actual specimens which have both selvages present, and which invariably have a width of approximate 50 cm. In the study of some large fragments where it has been possible to identify and to note meticulously the "faults", such irregularities seem to suggest either local accidents, such as miscellaneous shedding errors where the required warp ends failed to rise, or the omission or accidental reduplication of one or more sheds. The Han Dynasty figure harness were probably lacking any provision for automatic repetition in the width, and hardly ever repeating more than a small number of pattern sheds in the length, either because of the limitations of the apparatus, or the laboriousness of the procedures involved. It can thus be said that the wide pattern unit of Han silks suggest a figure harness of quite different type from the drawloom figure harness familiar in Europe which could make the fullest use of its ability to repeat a pattern in the width as well as the length of a textile (see Donald King, "Some Notes on Warp-faced Compound Weaves", Bulletin de Liaison, C.I.E.T.A., n° 28, Lyon 1968).

The earliest patterned silk, of apparently non-Chinese manufacture, which is known to us dates from the third century A.D. The fragment, measuring approximately 17 cm width x 8 cm length was found during a controlled excavation in Dura-Europos, on the banks of the Euphrates in Syria. The dating of this silk specimen, like all the other finds at this site, is associated with the fall of the city in approximately 256 A.D. This specimen is preserved in the U.S.A., in the Yale University Art Gallery. The woven ornamentation on the Dura-Europos silk consisting of a small geometrical angular pattern is inspired by a Greek or Near Eastern motif, frequently encountered on tapestries (a comparable example is the woollen specimen in tapestry technique from Noin-Ula). What however differentiates the Dura-Europos specimen from Chinese manufactured patterned silks of the Han Dynasty are two essential factors :

- 1) its ornamentation has been obtained not through the floated warp thread, but through the weft and
- 2) its yarn is in "schappe" (a silk yarn produced by

combing and spinning waste silk, after partial degumming) and not in "grège", which is the silk thread produced by reeling together the baves of several cocoons, is without twist and can be woven only in the gummed state. One can detect in the Dura specimen the presence of the main and the binding warp, and all threads have a heavy twist. The Han silks have grège threads and no appreciable twist.

Two other patterned specimens, dating from approximately the same period (or slightly thereafter), with the same fibre and weave characteristics as the Dura-Europos specimen were found by Stein in Lou-lan. All three finds mentioned above are important, for over a long period it had been assumed that weft-faced ornamentation was not employed until between the 5th and the 7th centuries. It was also assumed that weft-faced ornamentations were executed on the drawloom. The small repeat and the visible faults in the Dura-Europos specimen has incited Vial to believe that it was probably executed on a "pattern-rod" type of loom. As for the two Lou-lan specimens, speculation regarding the loom device is still being made by experts - for one thing the fragments are not wide enough to allow a clearly study of the repeats, or for that matter the repetition of the faults; it is therefore hard to determine the type of figure harness which was used for these two textiles (the two Lou-lan specimens have been discussed by me in 1) Archaeological Textiles, Irène Emery Roundtable on Museum Textiles 1974 Proceedings, The Textile Museum, Washington D.C., and 2) in Bulletin de Liaison, C.I.E.T.A., N° 41-42, Lyon 1975).

A common belief even now among many is that a number of the silk textiles which were preserved as wrappings of relics in European Churches, or have come from Egyptian graves, are to be dated from the fifth and sixth centuries A.D. Although devoid of any direct evidence of date or provenance, they are dated only on the basis of style. These silks, which also show a very high level of technical and artistic development are generally woven in a technique known as the "weft-faced compound twill", or "samit". There seems to be little doubt this weave technique was executed on a weaving apparatus which was similar to the drawloom. However, just when and where the drawloom was developed, and was first put to use still remains a matter of conjecture. Some claim it was developed in the Near East,

others in China. Dated evidences of textiles in this weave structure have only just begun to be grouped and analyzed, for it must be remembered that it is only in the last twenty years that excavations in the Soviet Union, particularly in the Northern Caucasus, and in mainland China have revealed to us a vast quantity of patterned silks. These textiles have been found under controlled circumstances and have valid dates. So far, judging from these archaeological finds there is very little which seems to suggest that intricate motifs in "samit" weave (for example the Sasanian type of pearled medallions enclosing various subjects) were in manufacture before the seventh century. On the basis of an important man's caftan found in the site of Mochtchevaya Balka in the Northern Caucasus, with a pattern of pearled medallions enclosing the simurgh (or senmurv) and dated to the eighth century, our present surmise is that fragments of a textile with a related design, preserved at the Musée des Arts Décoratifs in Paris and at the Victoria and Albert Museum in London, and which have been traditionally attributed a much earlier dating, should now be considered as falling within the same period as the caftan. In my article, jointly with Vial and Mme Meyer I have tried to show the technical evolutions which may indicate a time sequence in the manufacture of a group of silks with similar ornamentation (see my article, "A Newly Excavated Caftan from the Northern Caucasus" The Textile Museum Journal, Washington Textile Museum, Vol. IV, N° 3, 1976). I have however not been able to decide whether they were woven in Iran or Byzantium.

The development of the compound-weave techniques, starting with warp-faced compound tabby, warp-faced compound twill and changing to weft-faced compound twill was a progressive one and required changes in the figure harness or the loom system. While some of the weave techniques such as warp-faced compound tabby or twill were presumably manufactured on the same type of loom, namely the pattern-rod, it is possible that certain twill weaves and weft-faced compound tabbies were executed on a shaft loom with an added device, namely treadles. As of yet, however, in our study Vial and I have not been able to locate the specimen about which we can state with certainty that it was executed on a shaft loom with treadles.

I have already mentioned that the "samit" weave implies a technological breakthrough and the emergence of the drawloom. Patterned "samit" consists of two warps (one main

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warp and one binding warp) and at least two wefts. In the case of two wefts, one of them is used for the ground weave and the other is used for the pattern in the case of three wefts, one is used for the ground and the two for pattern, and so on). As a result the ground and the pattern are visible on the front of the fabric as a constant weft-faced twill. These wefts are always separated by the main warp ends which remain invisible on both sides of the fabric. At the same time, the binding warp binds the ensemble of wefts in twill (almost always in 2:1) effected by pass. The action of the drawloom required an assistant : a draw-boy was responsible for the raising of the main warp-ends by actioning the tail-cords (the groups of tail-cords were pre-selected or pre-arranged in accordance with the ornamentation which was to be produced); a weaver threw the shuttles and by means of treadles acted upon the heddels which raised the binding warp ends. Thus the draw-boy was responsible for the pattern and the weaver for the twill bind (this is already cited in my article, "A Newly Excavated Caftan . . .", 1976, pp. 29-30). It is extremely important in trying to determine the types of faults which are found on a specimen in this weave, to assess whether they were provoked by the action of the draw-boy or the weaver; as we have seen, one had the control of the main warp, while the other of the binding warp. It is for this reason that we feel that the manner in which technical terms are employed for defining weave structures are of the utmost importance, and in this the Vocabularies of Technical Terms evolved by C.I.E.T.A. published with expert help in seven languages represent a sourcework not to be neglected. We have noted that in a recent publication, an important group of patterned fabrics in the weft-faced compound twill weave have been described as having "a compound structure, a weft-faced twill weave with inner warps and complimentary wefts" (The Royal Hunter : Art of the Sasanian Empire, The Asia Society, Inc. 1978). While the description in itself is not inaccurate, it does not make specific the important and separate role of the main and the binding warps in the interlacing system of this weave. As is technically known, only the main warp ends remain invisible while the binding warp ends are visible. Also, it is essential to know in a precise way the number of wefts which have been used in a weft-faced compound twill specimen; it is also very important to know whether all the wefts were employed in a constant or an intermittent way. It has been Vial and my joint effort to try and make explicit a fact which has been already dealt with

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by eminent specialists such as Walter Endrei and Shinzaburo Sasaki, that a weave structure is directly associated with a weaving apparatus, and therefore cannot be analysed in dissociation with the action of the figure harness and the organisation of the loom. It must also be remembered that the question of *découpure* is fundamental for the understanding of the shedding mechanism. The study of all these factors in early Oriental textiles have thus enabled us to understand and to grasp some of the essential skills and virtuosity which characterize these beautiful patterned silks; however, some new investigations still remain to be done.

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PROPERTIES OF SOME ARCHAEOLOGICAL
TEXTILES

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

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ABSTRACT

As part of a major study of the conservation of degraded historic textiles, several mechanical and physical properties have been measured on archeological cotton mortuary wrapping cloths removed from Peruvian mummy bundles. Data is presented for yarn structure, count, twist, helix angle, twist factor, crimp and tenacity.

Yarns from different mortuary wrappings were surprisingly similar in construction and mechanical properties. High twist two-ply yarns were formed from relatively low twist singles resulting in a loss of the bulk observed in the singles yarns. A number of the yarns had helix angles from 40 to 50 degrees. This degree of twist no doubt contributed to the good strength observed in these eight hundred year old yarns. Weave crimp data indicate that the plain weave fabrics are warp faced.

INTRODUCTION

As part of a major study of the conservation of degraded historic textiles [1,2], several chemical, mechanical, and physical properties have been measured on archeological cotton samples. These materials include fabrics from the Peruvian Moche and Chancay Valley Sites, mortuary wrapping cloths, and seed cotton removed from Peruvian mummy bundles. The present paper is concerned mainly with fabric and yarn structural parameters such as crimp, count, diameter, twist, helix angle, twist factor and tenacity.

The cotton yarns examined were provided by Mr. James Vreeland of the Proyecto Julio C. Tello, Musea de Arqueologia y Etnologia, Lima, Peru. These yarns were taken from coarse textured plain weave fabrics found in a Peruvian mummy bundle dated approximately 1240 \pm 50 A.D. This bundle, weighing over 200 kilograms, was found in the Lince pyramid site in Lima, Peru. Dissection of the bundle revealed the mummy to have been a young woman, 18-20 years of age. The bundle also included over 150 kilograms of plain weave wrapping cloths, one of which measured more than 40 meters in length. This piece is the longest single fabric discovered in the New World from prehistoric times. A description of this mummy bundle is given by Vreeland [3].

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The 15 yarns received are listed in Table I. The number preceding the parenthesis is Vreeland's fabric specimen number, the letter in parenthesis designates warp (W) or filling (F) yarn, and the final letter identifies individual yarns removed from a single fabric. When possible, he removed the yarns from one meter lengths of cloth in both the warp and filling directions in order that fabric geometry could be determined using Peirce's model [4]. The length of fabric from which the yarn was removed is given by L_c .

All the yarns are spun from undyed white cotton fibers. The yarns have no perceivable finish. Thirteen of the yarns are two-ply and two [13(F)] are four-ply. This report considers only the two-ply yarns.

Setting up a program to test these yarns demanded the establishment of a comprehensive list of priorities. The amount of the archeological material was limited, and the goal was to extract as much information as possible from the finite supply of test material. While some characterization tests can be carried out without altering test yarns, most tests require at least some manipulation of the yarn while some require complete sacrifice of the tested material. The destruction of the material brought about by many of the tests made it imperative that the entire range of possible tests be considered and placed in some descending order of importance before testing began.

The samples were potential sources of two types of information - archeological and chemical. Since the analysis was being made primarily for archeological information, technological characterization assumed top priority. Fortunately the yarns and fibers remaining after most types of physical examination are still suitable for chemical testing.

The archaeologist has traditionally been interested in data concerning yarn number, denier or tex, evenness, twist direction, contraction due to twist, turns per inch, and twist helix angle for both the yarn and individual plies. This data plus information about fabric geometry, dyeing, finishing and ornamentation has formed the basis of most archeological textile analysis in the past [5, 6, 7]. As the scientific method of the archeologist has expanded, information about fiber fineness, color, lumen pigmentation, length distribution, maturity and cross sectional characteristics has also been sought [8]. These yarns also provide a unique opportunity to examine their bulkiness and level of twist. For this reason, twist factors were calculated. The tensile properties and moisture regain of the yarns are also of interest [9].

After the completion of physical testing and characterization, chemical tests to determine pH, degree of crystallinity, carboxyl content and carbonyl content will be

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conducted. This chemical information will guide the formulation of conservation procedures for the mummy cloth. Results of the chemical characterization will be reported at a later time.

In almost every case, the amount of yarn tested was perhaps too small to yield statistically valid information for fabric populations other than the one analyzed; however the data generated will hopefully give some sense of the characteristics and appearance of the samples. When the sample available was too small for use of existing test methods, the methods were adapted or other techniques developed. These problems are discussed as they occur in the following section on test methods.

YARN TESTING

Yarn length, crimp and contraction. The yarns were equilibrated at standard textile testing conditions, $70 \pm 2^\circ\text{F}$ and $65 \pm 2\%$ RH. In most cases these yarns were taken from one meter lengths of fabric. The length of fabric from which each yarn was removed is listed as L_C in Table I. The crimp factor of the weave can be determined from the equation

$$\text{Crimp } (\%) = 100(L_e - L_C)/L_C \quad (1)$$

where L_e = extended length of the yarn after removal from the fabric and L_C = contracted length of yarn in the fabric [10]. The contraction is calculated from the same data [10].

$$\text{Contraction } (\%) = 100(L_e - L_C)/L_e \quad (2)$$

Measurement of the extended yarn length presented some problems. By varying the tension placed on any one yarn, a variety of lengths could be obtained. Two methods for tensioning the yarn were used. When faced with the same problem, Bird opted for having the same person tension all the yarns during the measuring to insure a comparatively consistent result [11]. The lengths of yarn in this test are much shorter than those he worked with, but this principle was used for the first measurement. The yarn was manually extended until all the kinks were just pulled out and it was then measured. Since none of the yarns were particularly lively, kink removal was fairly straightforward. The results of this test are listed as L_e in Table 1. This method might be improved by having several people tension and measure the yarns and then average the results.

The second length measurement was made using a modification of a method given in ASTM Test Method D 1059 - 69 T [12]. The test specifies that the yarn be measured with a tension of 0.25 grams-force/tex. Tex was calculated from the formula

$$\text{Tex} = 1000 \text{ Yarn mass (g) / Yarn length (m)} \quad (3)$$

based on L_e 1 for the calculation. Use of the stress specified in this method meant attaching weights in excess of 50 grams to many of the yarns. In order to prevent inordinate stretching and possible deformation of the yarns, half the suggested stress was used. The yarns appeared well straightened under this stress. The results of this test are listed as L_e 2 in Table I. Crimp and contraction calculations for each set of length measurements follow these measurements in the table.

Yarn Diameter. All the yarns to be measured were comparatively large and of varying degrees of evenness. Diameter measurements were taken using a 7X measuring magnifier (Bausch and Lomb) with a scale divided into 0.1 mm divisions. Measurements were made at approximately 1 cm intervals along the length of the yarn. The average of the measurements, and the coefficient of variation are listed in Table I.

Denier, Tex and Cotton Count. The equilibrated yarns were weighed on a Mettler H18 balance. The yarn tex was determined from equation (3). Denier is 9 x tex and cotton count (cc) was calculated from the relation [12]:

$$cc = 5315/\text{denier} \quad (4)$$

The yarn weights, and estimated tex, denier and cotton count are listed in Table II. The small amount of each sample makes the precision of these measurements rather poor. Even in highly regular yarns, a longer length of yarn is desirable for any yarn number calculation. Handspun yarn can vary considerably in diameter and density. Yarn size information derived from shorter pieces cut from the yarns used for twist tests are presented in Table III. The yarn lengths, weights, deniers, tex, and cotton counts are all given along with the same information about the two plies that form the yarn. Comparison of these numbers with those of Table II gives some sense of the variation occurring within the sample.

Twist Direction, Turns per Inch, Helix Angle and Twist Factor. Twist direction and turns per inch (t.p.i.) were measured using ASTM Test Method D 1423 - 68 [12]. Since the yarns to be measured were irregular, twist was measured over a series of ten 1" segments rather than one 10" segment. Identical measurements were made on two 10" lengths of each yarn. Results of these tests are listed as series 1 and 2 in Table IV. The coefficient of variation listed along with the t.p.i. average reveals some of the yarn's irregularity.

Helix angle, also listed in Table IV, was calculated from the following formula [14]:

$$\tan A = \pi DT \quad (5)$$

where $T = \text{t.p.i.}$, $D = \text{diameter of yarn}$ and $A = \text{helix angle}$.

Twist direction and t.p.i. for the singles yarns comprising the plied yarns in series 1 are given in Table V.

Twist factor (τ) was calculated using the formula [13]:

$$\tau = \text{t.p.i.}/\sqrt{cc} \quad (6)$$

Conversion to the tex system is achieved by multiplying τ by 9.57. Twist factors are listed in Table V.

Tenacity. The breaking strengths of some of the yarns were measured on an Instron Tensile Testing Machine using ASTM Test Method D 2256-75 [12]. A one inch jaw separation was used. The breaking tenacities and the percent elongation and their coefficients of variation are listed in Table VI.

DISCUSSION

The yarns listed in Table I are all from the Lince mummy bundle. Yarns bearing the same number before the parenthesis (e.g., 1 or 13) are from the same fabric. Vreeland's designation system was retained so that the data could be readily related to that in his publications.

The fabric construction was plain weave for all the analyzed fabrics and warp faced in most cases. The yarn length data in Table I suggest that all the fabrics for which both warp and filling yarn measurements are available have warp face construction. Crimp factors for the warp range from 20.5% to 38.4% while filling yarns range from only 2.0% to 11.6%. This data would indicate warp faced fabrics since it is known that the materials are all plain weave.

Two methods were used to measure the decrimped length of short segments of yarn. Consistently shorter lengths were obtained for the hand tensioning measurements. In all cases, however, results of both methods were within a few percent of each other. Since the calculations made from these measurements are inexact at best, the easier hand tensioning method is recommended for similar measurements in the future. An average of a series of hand tensioned measurements of the same yarn could be taken and used for yarn and fabric calculations.

Yarn size using three different systems is reported in Tables I-III. Yarn number was calculated from yarn weight and length measurements. Here the accuracy of the length measurements has a crucial impact on the yarn number estimation. Increasing the length of yarn sample measured maximizes yarn number accuracy. Table II gives the size estimates for the entire original length of the yarn samples. Shorter pieces were

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then measured and weighed for yarn number comparison with the longer samples as shown in Table III. For hand spun yarns, results in Table III show good agreement with results in Table II. Table III also gives yarn number information for the individual singles yarns constituting the ply. While some yarns were plied from singles yarns of roughly the same yarn number, other plied yarns were twisted from yarns of widely dissimilar counts.

All the yarns were 2 ply and all but one were "S" twisted from "Z" spun singles. The one "S" twisted ply, formed from "Z" singles, came from a fabric that also contained two of the "Z" twisted plies. Without additional anthropological information, it might be inferred that the yarn for the fabric was the work of more than one spinner.

The amount of twist in the samples varied from yarn to yarn and also varied greatly within any one yarn. When handspinning, this twist variation can compensate for uneven ply thickness and thus serve to produce a uniform plied yarn. The individual singles also showed wide variations in t.p.i. The yarns exhibited high twist helix angles.

Twist factors for these yarns generally fall in the range of ring weft (32-35 tex^{1/2} turns/cm) and ring warp (38-43 tex^{1/2} turns/cm) cotton yarns. Some of the highest values compare with voile (49-53 tex^{1/2} turns/cm) and crepe (57-77 tex^{1/2} turns/cm) cotton yarns [13]. For interpretive comparisons, a tabulation of modern twist factors is given in Table VII. From Table VI it is evident that the singles yarns were spun with very low twist, even below that of the lowest twist commercial yarns produced today. This low twist yielded a soft, bulky singles yarn. The high bulk was somewhat negated, however, by the high twist factors of the plies as listed in Table V. If these fabrics, as Vreeland has suggested [17], were purposely constructed with the objective of obtaining high bulk or cover per unit weight, the spinners perhaps did not consider the effect of the high twist levels in the ply yarns. The other case might be, however, that the weak, low twist singles yarns could not be woven efficiently without the reinforcement provided by the higher ply twist.

The tenacity of some of the archaeological yarns is listed along with the tenacity of a comparable modern machine spun cotton yarn [14] in Table VI. Since yarn strength is related to a number of complex factors such as original fiber strength, method of spinning, twist factor, yarn size, and fiber interaction, a direct comparison of the archaeological specimens with the machine spun yarn must be made with caution. It would seem that the strength retention of the archaeological yarns is quite good. The healthy appearance of the yarns supports this conclusion. Further evaluation of yarn strength would be aided by fiber length, fineness, and tenacity data.

CONCLUSIONS

Two-ply cotton yarns taken from plain weave Peruvian mummy wrappings, ca 1240 + 50 A.D., have been analyzed. The information gathered about yarn length, diameter and twist describes yarn construction and also gives some information about fabric geometry.

Additional study to determine fiber characteristics such as fineness, length distribution and cross section appearance can be done as needed. Chemical tests to determine pH, D.P., moisture regain, carboxyl and carbonyl content will be conducted on both these samples and other archaeological specimens that are under study.

Hopefully, the physical characterization studies will benefit archaeologists. Any fabric and yarn technology information serves to increase the understanding of a culture that spun and wove some of the most beautiful textiles ever made.

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Table I. Length, diameter, crimp and contraction values for archaeological plied yarns

Yarn	L _c (cm)	L _e 1* (cm)	Crimp 1 (%)	Contraction 1 (%)	L _e 2** (cm)	Crimp 2 (%)	Contraction 2 (%)	Diameter	
								Mean (cm)	Coef. of var. (%)
44(W)A	100.0	126.8	26.8	21.1	129.5	29.5	22.8	0.0800	23.9
44(W)B	100.0	125.5	25.5	20.0	126.2	26.2	20.8	0.1230	22.7
44(W)C	100.0	128.0	28.0	21.9	130.5	30.5	23.4	0.1010	18.8
1(F)A	100.0	111.6	11.6	10.4	113.1	13.1	11.6	0.1102	29.0
1(W)A	100.0	125.7	25.7	20.5	126.4	26.4	20.9	0.1122	29.4
1(W)B	100.0	124.1	24.1	19.4	126.8	26.8	21.1	0.0940	23.5
13(W)A	100.0	130.4	30.4	23.3	131.9	31.9	24.2	0.0910	19.8
13(W)B	100.0	138.4	38.4	27.8	140.0	40.0	28.6	0.0881	20.8
21(F)A	50.0	51.0	2.0	2.0	51.6	3.2	3.1	0.1070	17.9
21(W)A	100.0	124.1	24.1	19.4	124.6	24.6	19.7	0.0980	12.2
29(W)A	100.0	120.5	20.5	17.0	121.8	21.8	17.9	0.1052	19.8
29(W)B	100.0	122.0	22.0	18.0	123.4	23.4	19.0	0.1050	26.6
29(F)A	100.0	106.0	6.0	5.7	106.9	6.9	6.5	0.0990	27.2
13(F)A	100.0								
13(F)B	100.0								

* Measured using the hand tensioned method

** Measured using 0.25 gf/tex tensioned method

Table II. Measured weights and lengths of the archaeological plied yarns and calculated yarn sizes

Yarn	Mass (g)	Length 1* (cm)	Denier	Tex	Cotton Count	Length 2** (cm)	Denier	Tex	Cotton Count
44(W)A	0.2158	126.8	1532	170.2	3.47	129.5	1500	166.6	3.54
44(W)B	0.3939	125.5	2825	313.9	1.88	126.2	2809	312.1	1.89
44(W)C	0.2769	128.0	1947	216.3	2.73	130.5	1910	212.2	2.78
1(F)A	0.3565	111.6	2875	319.4	1.85	113.1	2837	315.2	1.87
1(W)A	0.3075	125.7	2202	244.6	2.41	126.4	2189	243.3	2.43
1(W)B	0.2330	124.1	1690	187.8	3.15	126.8	1654	183.8	3.21
13(W)A	0.3075	130.4	2122	235.8	2.50	131.9	2098	233.1	2.53
13(W)B	0.2023	138.4	1316	146.2	4.04	140.0	1301	144.5	4.09
21(F)A	0.0996	51.0	1758	195.3	3.02	51.6	1737	193.0	3.06
21(W)A	0.1833	124.1	1329	147.7	4.00	124.6	1324	147.1	4.01
29(W)A	0.1763	120.5	1317	146.3	4.04	121.8	1303	144.8	4.08
29(W)B	0.2408	122.0	1776	197.4	2.99	123.4	1756	195.1	3.03
29(F)A	0.1681	106.0	1427	158.6	3.72	106.9	1415	157.3	3.76

* Measured using the hand tensioned method

** Measured using the 0.25 gf/tex tensioned method

Table III. Weight, length and yarn size of short lengths of plied yarns and their singles constituents

Yarn	Length* (cm)	Mass (g)	Denier	Tex	Cotton count
<u>Plied Yarn</u>					
44(W)A	25.4	0.0450	1590	177	3.34
44(W)C	25.4	0.0505	1789	199	2.97
1(F)A	25.4	0.0740	2622	291	2.03
1(W)A	25.4	0.0650	2303	256	2.31
1(W)B	12.7	0.0202	1432	159	3.71
13(W)A	25.4	0.0368	1304	145	4.08
13(W)B	25.4	0.0374	1325	147	4.01
21(F)A	12.9	0.0224	1563	174	3.40
21(W)A	25.4	0.0461	1634	182	3.25
29(W)A	25.4	0.0453	1605	178	3.31
29(W)B	25.4	0.0434	1538	171	3.46
29(F)A	25.4	0.0337	1194	133	4.45

Single Yarn #1 in the ply

44(W)A	27.3	0.0218	718	80	7.40
44(W)C	27.0	0.0256	854	95	6.23
1(F)A	26.6	0.0313	1059	118	5.02
1(W)A	26.0	0.0278	961	107	5.53
1(W)B	13.3	0.0063	425	47	12.50
13(W)A	26.7	0.0183	618	69	8.61
13(W)B	26.4	0.0179	611	68	8.69
21(F)A	13.0	0.0124	857	95	6.20
21(W)A	26.7	0.0193	651	72	8.16
29(W)A	26.4	0.0185	632	70	8.41
29(W)B	26.0	0.0212	733	81	7.25
29(F)A	27.0	0.0107	357	40	14.90

Single Yarn #2 in the ply

44(W)A	27.62	0.0230	749	83	7.09
44(W)C	26.67	0.0252	850	94	6.25
1(P)A	26.70	0.0425	1433	159	3.71
1(W)A	25.72	0.0374	1309	145	4.06
1(W)B	12.78	0.0140	986	110	5.39
13(W)A	26.99	0.0184	614	68	8.66
13(W)B	26.04	0.0202	698	78	7.61
21(F)A	12.93	0.0100	696	77	7.64
21(W)A	27.31	0.0264	870	97	6.11
29(W)A	26.67	0.0264	891	99	5.97
29(W)B	28.09	0.0222	711	79	7.47
29(F)A	27.31	0.2218	731	81	7.27

* Measured using the hand tensioned method

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Table IV. Twist measurements on archaeological
plied yarns

Series 1					
Yarn	Ply Twist Direction	t.p.i.	No. of Measure- ments	Coeff. Var.(%)	Helix Angle (°)
44(W)A	Z	10.1	10	16.8	45.0
44(W)C	S	-	-	-	-
1(F)A	S	3.8	10	24.7	27.4
1(W)A	S	10.9	10	23.6	56.6
1(W)B	S	5.1	10	42.8	30.7
13(W)A	S	9.1	10	16.9	45.7
13(W)B	S	-	-	-	-
21(F)A	S	7.9	10	18.5	46.1
21(W)A	S	10.4	10	38.9	51.6
29(W)A	S	5.3	10	27.0	34.6
29(W)B	S	-	-	-	-
29(F)A	S	7.4	10	19.5	42.1

Series 2**					
Yarn	Ply Twist Direction	t.p.i.	Helix Angle (°)	Twist Factor	
				t.p.i. Vcc	Tex turns cm
44(W)A	Z	11.1	47.7	6.1	58
44(W)C	S	9.5	49.9	5.5	53
1(F)A	S	4.4	31.0	3.1	30
1(W)A	S	5.7	38.4	3.8	36
1(W)B	S	7.3	40.3	3.8	36
13(W)A	S	8.7	44.4	4.3	41
13(W)B	S	8.4	42.5	4.2	40
13(W)B	S	7.3	43.9	4.0	38
21(W)A	S	6.5	78.3	3.6	35
29(W)A	S	7.4	43.9	4.1	39
29(W)B	S	9.8	51.8	5.3	51
29(F)A	S	8.1	44.7	3.8	36

* Series 1: Twist was measured in a series of ten 1" segments

** Series 2: Twist was measured in one 10" segment

Table V. Twist measurements on singles yarns from archaeological plied yarns

Yarn	Twist Direction	t.p.i.	No. of Measure- ments	Coeff. of Var. (%)	Twist Factor	
					t.p.i. \sqrt{cc}	$\sqrt{\text{tex turns}}$ cm
44(W)A	single 1	4.1	10	37.5	1.5	14
	single 2	5.9	10	43.4	2.2	21
1(F)A	single 1	5.5	10	46.7	2.5	24
	single 2	5.4	10	58.9	2.8	27
1(W)A	single 1	16.6	10		7.1	68
	single 2	4.1	10	14.9	2.0	19
1(W)B	single 1	4.9	10	56.3	1.4	13
	single 2	3.0	10	121.0	1.3	12
13(W)A	single 1	5.6	10	41.3	1.9	18
	single 2	6.2	10	51.5	2.1	20
21(F)A	single 1	3.1	10	74.2	1.2	11
	single 2	5.9	10	30.2	2.1	20
21(W)A	single 1	6.6	10	61.1	2.3	22
	single 2	5.3	10	73.3	2.1	20
29(W)B	single 1	5.2	10	64.4	1.9	18
	single 2	4.9	10	66.3	1.8	17
29(F)A	single 1	5.1	10	31.2	1.3	12
	single 2	3.5	10	122.0	1.3	12

Table VI. Tenacity of some archaeological plied yarns

Yarn	No. of Measure- ments	Tenacity (gf/den)	Coeff. of var. (%)	Breaking Elongation (%)	Coeff. of Var. (%)
44(W)A	3	1.01	0.09	15.00	0.1
1(W)B	3	0.56	0.41	8.67	0.4
13(W)A	3	0.61	0.02	15.67	0.1
21(F)A	3	0.47	0.33	11.65	0.2
21(W)B	3	0.91	0.25	14.50	0.1
29(F)A	2	1.05	0.17	18.03	0.1
Modern machine spun cotton yarn, 10's [16]		1.33			

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Table VII. Twist factors for commercial textile yarns [13,15]

End Use	Singles Yarn Size (cc)	Twist Factor in Singles (t.p.i./ \sqrt{cc})	Ply Yarn Size (cc)	Twist Factor in Ply (t.p.i./ \sqrt{cc})
Knitted hosiery combed and mercerized	40	3.3	20	4.7
Bedspread tufting	8	4.7	4	1.9
Industrial sewing thread	12	5.5	4	9.5
Fire hose	8	4.5	0.73	3.9
Knitting yarns		2.5 - 3.5		
Filling yarns		3.5 - 4.5		
Warp yarns		4.0 - 5.5		
Doubling weft		3.0 - 3.3		
Ring weft		3.3 - 3.6		
Ring warp		4.0 - 4.5		
Voile		5.2 - 5.5		
Crepe		6.0 - 8.0		

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A STUDY OF MICROFLORA OF MUSEUM TEXTILES
AND METHODS OF THEIR DISINFECTION AND
PROPHYLAXIS

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A STUDY OF MICROFLORA OF MUSEUM TEXTILES AND METHODS OF
THEIR DISINFECTION AND PROPHYLAXIS

N.L. Rebrikova

Much attention has been given to the problem of biological destruction of textiles in industry. However, up to the present there have been practically no studies purporting to determine the fungus species that attack textiles of museum collections, nor any attempt has been made to develop a safe and effective procedure of their disinfection and prophylaxis.

Museum textiles, which are works of applied art, are a very favourable substrate for the development of various microorganisms including fungi because it is cellulose and proteius that form their structural backbone. Of the attacking microorganisms those are considered most dangerous that enzymically split and assimilate such natural polymeres as cellulose and keratin. Sometimes those microorganisms develop thanks to certain secondary substances, e.g. various impurities, dressings, size, etc. without causing significant changes of fibre. To preserve museum textiles in a good condition it is important to avoid those substances, especially impurities, because the stains left by fungi impair the outward appearance of an object, and it is practically impossible to remove them without damaging the fibre.

In order to determine the fungi species that attack textiles under unfavourable conservation condition in 1973-1977 collections of sixteen museums situated in different climatic zones were investigated. As a result, some most typical representative of microflora, developing on textiles have been determined.

It has been established that fungi attack textiles made of natural fibre either of vegetable or animal origin. Sixty fungi species belonging to sixteen genera were isolated. A study of mould distribution on different natural fibres revealed no clear correlation between the fungus and the fiber type. The most widespread fungi occurred on fibres of all types. Textiles made of vegetable fibres exceeded others in the variety and quantity of fungi, they were followed by silk, and, finally, by wool. The following fungi occurred most frequently: *Penicillium purpurogenum*, *Penicillium cyclopium*, *Aspergillus versicolor*, *Penicillium decumbens*, *Penicillium chrysogenum*, *Aspergillus ustus*, *Penicillium funiculosum*, *Cladosporium herbarum*, *Aspergillus flavus* and some others.

The study revealed that fungi attacking textiles are powerful chromogenic agents whose growth is accompanied by the formation of stains of various colours, or else they have a dark mycelium which penetrates into fibres changing colour of textiles. However, fungus activity, besides impairing textiles' outward appearance leads to reduction of durability and, eventually, to total destruction, which is a result of utilization of natural polymeres by fungi. The theory that fungi feed exclusively on natural fibre was discussed in the literature, but no definite conclusion has been arrived at, especially with respect to animal fibres.

Therefore, a number of fungus strains were tested for ability to utilize natural fibre, with the aim of determining the most destructive agents. The fungi isolated from textiles actively attacked cellulose. One strain, namely, *Cladosporium sphaerospermum* was especially active causing reduction of durability of a specimen (linen) by 40%. Animal fibres were, on the whole,

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more fungus - resistant Durability of wool did not change within the experimental error. Silk proved to be more resistant than linen, with the exception of one very active strain, viz. *Penicillium purpurogenum*. It was thus shown that some strains cause considerable destruction of fibres. Some of the fungi isolated did not affect fibre durability. It seems that they can develop on textiles owing to the presence of such secondary substances as size, dressings and impurities.

It was noted, in the course of the investigation, that cultural attributes of the isolated strains are subject to change. In the identification of molds a scanning electron microscope was used, which allowed to obtain more specific data on the morphology of penicillus conidia and to make some corrections in the diagnosis of the species studied. Penicilli of the *Bi-verticillata-Symmetrica* section were investigated and changes of cultural attributes used in taxonomy were traced subject to the environmental changes.

A number of substances were tried as disinfectants and conservation agents, such as fluorinated organosilicon compounds and quaternary ammonium compounds (QAC). The former proved to be rather ineffective as fungicides. As to QAC, their fungicide activity was observed both in solutions and on textile samples. The advantages of QAC in practical usage are the following: their solutions are colourless, they do not interact with fibre, are soluble in water and organic solvents, the surface activity of their solutions increases their washing and softening effect besides, they are highly active bactericides and fungicides and the range of their activity is very wide.

Five compounds of the QAC group were tested by the bowl method normally used for textile anticeptics.

Within this method the activity of anticeptics and the stability of fungi can be evaluated by the width of the zone around textile samples impregnated with anticeptics, where the growth of fungi is retarded, as well as by an estimation of state of the environment over the samples, expressed in numbers.

Catamin AB (alkyldimethylbenzinammonium) proved to be the most active anticeptic. Its overall zone of growth inhibition in all the tests was largest. Alarmin (alkydiethylbenzinammonium) was slightly less powerful. The most stable fungus among those investigated was *Tichoderma viride* whose zone of growth inhibition was smallest. Also, fibre type had a noticeable effect on the results of the experiment. The most active anticeptics (catamin AB and alarmin) were then selected and an attempt was made to determine the optimum conditions of their application as disinfectants, which would approximate real conditions. The best results were obtained with 1% solutions (at a temperature of 40°C, exposition time of 30 min, and bath module of 1:50).

The tested QAC compounds also showed lasting residual activity which makes it possible to use them as conservation agents. Textiles impregnated with those anticeptics preserve their antifungal properties for quite a long time (one year or longer).

New anticeptics for textile disinfection and conservation must be thoroughly tested for absence of damaging effects upon objects. Therefore an experiment has been carried out to determine to what extent the QAC compounds affect colour of the dyes that had been used before the discovery of anilin dyes. The data obtained directly after the anticeptics had been applied and in the process of ageing showed that if used in concentrations recommended the anticeptics affect the

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quality of textiles only insignificantly.

At present in textile restoration starch glue is usually used, protected with natrium pentachlorcarbolate. However, this anticeptic causes changes in glue colour, so a new anticeptic, viz. nipagin (methyl benzine carboxylic) was tested. Glues containing 2% of nipagin (of starch weight) proved to be as fungus - resistant as glues containing the same amount of natrium pentachlorcarbolate. Nipagin does not change colour of glue and less affects organic dyes; for these reasons it can be recommended in place of natrium pentachlorcarbolate.

STONE

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Programme 1975-1978

1. Critical review of literature on causes of weathering, effects of treatment, weathering on conservation of stone (continuation) (Stambolov, in collaboration with Van Asperen de Boer).
2. Study on weathering of stone in monuments:
 - in general (Torraca);
 - in details:
 - a) artificial weathering by means of soluble salts (Tabasso);
 - b) evaluation of weathering by means of porometry (Rossi-Doria);
 - c) weathering influenced by organisms (Giacobini);
 - d) weathering of stones in monuments of Venice, under influence of environment / application of treatment techniques - cleaning, consolidation and filling (Musumeci, in collaboration with K. Hempel);
 - e) weathering of marly limestones in monuments of Venice - proposed methods of consolidation (Lazzarini).
3. Study on consolidation of stone in details:
 - a) soft clay-sandstone by means of precipitation of silicone (Penkala);
 - b) porous stone by means of monomers polymerized inside of stone with gamma-rays (Ramière);
 - c) sand- and limestone with silico-organic compounds (Materna);
 - d) soft and porous stone with silico-organic-silicates / treatment in situ and hydrophobization (Iakachvili);

- e) porous stone and clay in museum objects with solutions of polymers (Gerassimova).
4. Study on efficacy of treatment:
- a) preserving methods against capillary and condensation humidity (Moraru);
 - b) conservation of stone sculptures in outdoor exposition (Rossi-Manaresi);
 - c) impregnation, consolidation and filling of porous, soft stone in museum objects (Ageewa).

RECENT EXPERIENCE IN CONSERVATION OF STONE OBJECTS.

(ACTIVITIES AND ACCOMPLISHMENTS OF WORKING GROUP STONE)

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Abstract.

At its 4-th Triennial Meeting in Venice- 1975, the Working Group "Stone" has accepted the modified programme developing activities in the conservation of stone objects in museums, collections and from excavations. Consideration is also devoted to preserve outdoor objects and to consolidate decayed stone.

The activities and accomplishments of the Working Group "Stone" are reported on the background of world evolution in stone conservation during past three years. They are concerned mainly with complex conservation of valuable artistic and historic stone objects, consolidation of decayed stone, desirable characteristics of chemicals used in conservation of stone objects, protection of stone by means of water-repellency and organic surface layers, polymers coatings used for cleaning of dirty and stained surface of stone, mathematical model for computation and device for measurement of weathering rate of stone as well as documentation and inspection of treated stone objects.

-

The conservation of stone has a long tradition among activities of the ICOM-Committee for Conservation and already before 1963 in former ICOM-Committee for Scientific Museums Laboratories. In 1966 ICOMOS has organized its own Committee for Conservation of Stone. The Working Group Stone of ICOM-Committee for Conservation collaborates of course closely with this Committee since its formation.

At the 4-th Triennial Meeting of ICOM-Committee for Conservation in Venice - 1975, the Working Group "Stone" has adopted the new programme modified following the recommendation of Directory Board. This modification is involved in the development of methods applied in conservation of stone in museums, in collections and from excavations. An important consideration is devoted to preserve of stone objects in outdoors exposition and to consolidate decayed stone.

Stone objects in museum or collection may or may not be works of art. In evaluating objects it is necessary to determine the authenticity, its artistic and historic value as well as other individual features. Each interesting piece comes to be recognized, scheduled and documented. The scientific and technical aspects of conservation should be interconnected with historical and artistic factors in the aim to avoid damage to the integrity, genuineness and beauty of object. The aspect of original object, of its characteristic and decorative elements that remain must be strictly protected. Sometimes alterations not too readily visible may be tolerated. A satisfactory conservation should fulfil certain conditions as that it should be effective in arresting decay, durable in its protective behavior, changing as little as possible the appearance of the object, reversible, adapted to the particular nature and condition of object.

Before we go to the questions of actual repair and restoration it is well remember other fundamental principle for conservation work on stone objects. The objects may be classified according to their conditions of exposure. There are three characteristic groups:

- a/ Outdoor objects.
- b/ Sheltered objects.
- c/ Indoor objects - build up or protected inside.

The common factor in almost causes of deterioration is the presence and action of water. Therefore stone object must be protected as far as possible against all kinds of moisture. The outdoor object most urgent need as first aid measure, may be for protection, either by some form of natural or artificial shelter, or even by its transfer into interior.

As in other branches of the conservation of artistic & historic objects the conservation of stone consists in an adequate system of examination and diagnosis, protection against damaging agents and treatment, documentation followed up by periodic observations and inspection. It requires knowledge as well as experience.

Examinations and diagnosis:

In advanced examinations carried out in museums scientific laboratories the first aim is to identify object, to determine its composition, structure, material constituents- and the second one is to define its material condition, state of preservation, influence of environmental and climatic factors causing changes in stone object.

Accurate identification of stone requires mineralogic and petrographic examination which should be carried out by educated and experienced petrograph only. Determination of its physical and technical properties requires about 20 various examinations. Working Group of ICOMOS-Committee for Conservation of Stone under the presidency of M. Mamillan recommended 17 various determinations as standard methods of examination for stone objects. Determination of chemical composition of stone requires about 20 qualitative and quantitative analysis also.

Our knowledge of weathering processes of stone has considerably advanced during the last decade. The interpretation of chemical weathering may be quite satisfactorily, at least as regards common rocks and hence enable us to understand the degradation of stone objects. The weakest point of our interpretation concerns not mechanism, but the rate of alteration. It is certain that it depends on many factors influencing the rate of weathering of the stone and therefore there are many various parameters to measure. It seems necessary to reduce their number and to simplify the interpretation of results and the diagnosis of stone objects. Colleagues O.I. Katsinadze and T.V. Iakashvili present very interesting report on the study based on Veyerstrass theorem concerning mathematical model and device for the measurement and computation of the weathering rate of stone.

An other study on dependence between the rate of weathering, heat of moistening, specific surface and pH = reaction of stone is continued at Chemical Laboratory of National Museum in Poznań. This enables us to calculate the ratio and speed of alteration, especially in the case of presence of salts in stone. The same data provide facilities to evaluate the efficacy of treatment.

Cleaning.

Many authors divide the treatment of stone object into three main sections - cleaning, consolidation and protection. In the section cleaning we have an interesting contribution of colleagues - E. Melnikova and M. Lebel consisting in applying of polymer coatings for cleaning of dirty and stained stone surface.

Consolidation.

Most reports prepared for 5-th Triennial Meeting of the ICOM-Committee for Conservation, Working Group "Stone" concern consolidation of stone objects. For strengthening fragile stone one may adopt a method of deep impregnation using natural or synthetic media. Small fragmented or broken objects may be reassembled by using various methods and cementing or gluey materials. Some colleagues report examples of complex conservation of valuable stone sculptures comprising substantial, technical bearings on completion of fragmented and broken objects.

Another colleagues reported on application of modern mono and polymers for deep impregnation of decayed stone. Stone consolidating chemicals and processes were applied as far as 150 years ago. Each recommended process had to improve the strength of stone considerably with no limits of time. In view of such expectation obtained results were rather unsatisfactorily, especially in the case when solutions of silicates and fluosilicates were applied for porous stones in out of doors exposition.

Since many centuries natural organic resins, waxes and oils have been used in maintenance and conservation of stone objects. The efficiency of such treatment was rather good for inside exposed objects; in the case of outdoor objects there were frequently mentions of failure after relatively short period of time.

There are also many good results in applying of synthetic resins for conservation of indoor stone objects. These quite satisfactory results brought about many attempts to produce resins and to elaborate methods for their applying for decayed stone in out of doors exposition. Some specialized manufactures supply ready made brewages provided for consolidation and preservation of stone. Sandstone and limestone that are permeable and exposed outdoors are consolidated nowadays mostly with brewages based on silicon resins. Such brewages contain usually silicon resin dissolved in mixture of organic solvents modified by addition of silicon esters, acrylic, epoxy or polyurethane resins in the aim to improve their penetration and cohesive power. Because the penetration a polymer solution must be diluted and applied many times or in special procedure before an sufficient deep penetration and consolidation attained. A special application of acrylic is based on impregnation with monomers. Object saturated with monomer is then put to the radiation with gamma-rays from nuclear source.

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New invention in development of application of acrylic monomers for consolidation of stone objects shows the tendency to have the use of polymerisation at lower temperature by using accelerators of polymerisation e.g. BMA /di-methyl-amine/ or AIBN /azo-bis-isobutyronitrile/, together with initiator BPO /benzyl peroxide/. A very interesting study on this subject is reported by colleagues from Institut Royal du Patrimoine Artistique - Brussels, E. de Witte and M. Mathot.

Many conservators prefer solutions of polymers than monomers, because one can easier assort products which are wanting with respect to one or more desirable characteristics. Desirable characteristics of chemicals used in conservation of stone objects are studied in recent years by ICOM, ICOMOS, ICC-Rome Working Group on the Treatment of Stone, Working Group of German Chemists, Conservators and Mineralogists under the auspices of ICOMOS-National Committee of G.D.R..

Our working Group collaborates in this subject and has some new contributions in this topic, namely reports on behaviour of polybutyl methacrylate and copolymer BMA 5 in the treatment of limestone, elaborated by colleagues E.N. Ageeva, N.G. Gerasimova, M.N. Lebel and E.P. Melnikova. An other report elaborated by colleagues R. Bilinski and B. Penkala deals with properties of the macromolecule polyvinyl acetate and its application for the preservation of ancient stone objects.

Protection.

The third section of treatment - protection comprises environmental and surface preservation. The appropriate modification of aggressive environmental conditions in situ or even transfer of stone object to a controlled climate indoors are the most effective and right way of protection for almost stone objects with exception of pieces considerably contaminated with soluble salts. When present in stone, soluble salts can do more damage to an object of art or history, than perhaps any other factor. Damage causing by soluble salts may be as follows: the efflorescences in various forms of crystalline agglomerations, hard and brittle crusts, cracks and fissures, loss of cohesion of stone. The primary factor responsible for stone decay in that case is the hygroscopic nature of certain salts contaminating stone. The salt, dependant on its kind and the degree of its hydration has to be in relative equilibrium with humidity of the surrounded air. To do this it takes in /or gives up/ water as the humidity changes. Decay of stone is effected then by chemical and physical processes. Physical processes generate mechanical stresses which result in cracking, cleavage

and disruption of the porous structure of stone. Chemical processes consist in hydrolysis, acidity or alkalinity, oxydation or reduction and bring about in dissolution, decomposition, precipitation and deposition of transformed mineral constituents of stone.

Any attempt to stop processes caused by accumulation of soluble salts in stone without identifying and removing them are doomed to failure.

Surface protection of stone is based on hydrophobisation or protective organic layers and films. Nowadays the opinion is that dilute solutions of silicon resins and silicon rubbers in organic solvents are the best water-repellents for stone to protect it against rain water. Such dilute solution is not efficient as consolidant at all. It doesn't protect stone against ground water and humidity in form of fog, dew and white frost. Hydrophobisation has additional very precious virtues that it doesn't change original appearance of surface by no manner and makes stone resistant against dirt. That is the reason why water-repellents are more suitable protecting agents than any layers or films.

Surface layers have been frequently applied in the past for protective and decorative purposes to stone objects. Wax, paraffin, linseed oil, tallow, soaps-pigmented or not-pigmented are mentioned in old literature. Recently come to be used media and paints based on synthetic resins, mostly in the form of aqueous dispersion, sometimes as solutions in organic solvents. Sometimes they are used for renovation of dirty stone plates covering modern buildings.

Opinions on efficiency of protective layers and on correctness in applying for ancient objects are quite mixed. Strong reservations are held against their use for conservation of ancient stone objects.

Documentation and inspection.

Our working Group took little interest in documentation and periodical inspections of treated objects. Maybe some forms of collaboration with Working Group Documentation would be effective in order to elaborate an uniform system of documentation for conservation of stone objects and to coordinate it with adequate systems of documentation kept in museums and institutions dealing with treatment and protection of monuments and objects of art and history.

The long-time experience proves that all treatments of stone have a limited useful life and their length isn't possible to foresee. Periodical inspections of treated objects are required in order to verify applied methods, to detect in good time the end of efficiency of the treatment and to correct possible mistakes.

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THE CONSOLIDATION OF TUFF OF MAASTRICHT
BY IN SITU FREE RADICAL POLYMERIZATION
OF ACRYLICS

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5th Triennial Meeting
Zagreb, 1978

THE CONSOLIDATION OF TUFF OF MAASTRICHT BY IN SITU FREE
RADICAL POLYMERIZATION OF ACRYLICS

E. de Witte and M. Mathot

SUMMARY

The possibility of consolidation of small stone objects by impregnation with acrylates and free radical polymerization is investigated. As impregnation agent a mixture of methyl methacrylate and ethyl acrylate (50/50) is used.

The influence of monomer concentration, initiator concentration and polymerizing temperature was investigated. Neither the degree of impregnation, nor the initiator concentration seemed to have any major interest, but polymerizations carried out at different temperatures showed that the temperature is the most important factor which has to be taken into account. Temperatures higher than 65° C are necessary to obtain good results. Hardness tests and porosity tests show the improvement of the physical properties of the treated samples.

1. Introduction;

In a previous paper (1) we compared three consolidation methods for tuff. The impregnation with Paraloid B 72 was compared with the impregnation with a mixture of methyl methacrylate and ethyl acrylate (50/50), followed by a)

-ray polymerization and b) free radical polymerization. The results showed that the latter method merits more interest. In this paper we investigate whether it is possible to consolidate in a simple and cheap way relatively small objects in stone by free radical polymerization.

Tuff of Maastricht was used to carry out all experiments. It is a very soft limestone, quarried in Belgium and the Netherlands. Because of its softness, it is very liable to chemical and biological alteration, despite of which it has been used in building many Gothic and Roman churches (2).

2. Consolidation procedures.

2.1. Impregnation.

All impregnations were carried out in a vacuum desiccator on cubic samples of 5 cm edge. The sample was placed in a glass vessel in the desiccator and the pressure reduced to 10 mm Hg. By means of a 3-way tap the impregnating liquid was allowed to drop very slowly on the sample. The introduction of liquid was stopped when it seemed to start flowing out of the sample. Air was then admitted into the desiccator. The sample was wrapped immediately into aluminum foil to avoid evaporation. After weighting of the impregnated sample, it was put in an oven and the polymerization was started.

2.2 Polymerization.

The monomer mixture used to impregnate the samples, was an equimolecular mixture of commercial grade methyl methacrylate and ethyl acrylate. As free radical initiator, azo-bis-iso-butyronitrile was added. The commercial grade of this product had been recrystallized from aqueous methanol.

2.3. Influence of monomer concentration.

In our previous paper we carried out two batches of free radical polymerization. The samples of the first batch showed superficial cracks, those of the second batch were intact. As the degree of impregnation could cause the appearance of the cracks, the influence of monomer concentration was investigated.

A series of polymerizations with varying monomer concentration was carried out. The initiator concentration was 0.5 mole% and the polymerisation temperature 50°C. The results are summarized in table 1.

<u>g.mon.</u> <u>g.stone</u>	<u>% mon.lost</u> <u>during polym.</u>	<u>polym.time</u> <u>(hours)</u>	<u>appearance</u> <u>after polym.</u>	<u>result</u>
0.353	26.49	43	cracks	+
0.353.	13.50	43	cracks	+
0.351	25.45	43	cracks	+
0.330	16.53	60	cracks	+
0.252	16.53	60	cracks	+
0.231	19.58	44	cracks	+
0.219	90.79	60	unchanged	-
0.216	94.01	60	unchanged	-
0.188	85.65	44	unchanged	-
0.178	51.29	60	unchanged	-
0.174	98.47	60	unchanged	-
0.119	73.13	44	unchanged	-

Table 1 : Influence of monomer concentration.

+ : polymerization took place

- : no polymerization of the monomers

From table 1 it can be concluded that at an impregnation degree below 0.230 g mon/g stone no polymerization of the monomers takes place. Above this concentration the monomers polymerize, but cause cracks in the surface of the samples.

By changing the monomer concentration, it seems to be impossible to realize a good impregnation, without the appearance of cracks.

2.4. Influence of initiator concentration.

In order to see if the initiator has any influence on the polymerization behaviour of the monomer mixture, polymerizations with initiator concentrations of 0.5, 0.75

and 1 % were carried out. The results were identical to those in 2.3.

2.5 Influence of the polymerization temperature.

Polymerizations with 0.5 mole% initiator were carried out at 50, 60, 65 and 80°C. The results are summarized in table 2.

pol. temp ° C	g. mon, g stone	% mon, lost	g polym g stone	appearance after polym	results
50	0.353	26.49	0.259	cracks	+
60	0.355 0.235	28.90 90.56	0.252 -	unchanged unchanged	+
65	0.346 0.338 0.187 0.182	25.29 34.00 14.72 18.00	0.258 0.223 0.159 0.149	unchanged unchanged unchanged unchanged	+
80	0.258 0.247	31.54 27.50	0.176 0.179	unchanged unchanged	+

Table 2 : Influence of the polymerization temperature.

+ : polymerization took place

- : no polymerization of the monomers

Table 2 shows clearly that it is the temperature which influences mostly the polymerization behaviour of the monomer mixture. At 65°C, the degree of impregnation has no more any influence. At any monomer concentration, the polymerization will result in a good consolidation, without the appearance of any cracks. Increasing the temperature above 65° C will only result in speeding up the reaction, accompanied by a greater loss of monomer.

2.6. Polymerization at room temperature.

A well known method for the polymerization of vinyl monomers at room temperature is the use of benzoylperoxide (BPO) as initiator and di-methyl amine (DMA) as accelerator. We also tried this method for the consolidation of tuff.

2.6.1 Determination of the initiator mixture.

In order to see which is the best proportion of DMA which has to be added to the BPO-monomer mixture, a series of tests was carried out. To a mixture of 0.055 mol monomer and 0.5 mmol of BPO, 3, 4, 5, 6 and 8 drops of DMA was added.

Only the sample with 4 drops gave good results. In all other cases the polymer was of too low molecular weight.

2.6.2 Consolidation of samples.

The mixture which gave the best results in 2.6.1 was used to carry out the consolidations.

The samples were impregnated till saturation. The 5 samples treated this way were well consolidated and did not show any cracks. About 20 % of the monomer was lost during the polymerization. With isooctane it was possible to extract 35 % of the initial impregnated monomer. This is a slight disadvantage against the thermal polymerization, where it is not possible at all to extract any monomer after the polymerization. The appearance of the samples was also drastically changed. Where a consolidation normally gives the treated object a "wet" aspect, the consolidation with this method resulted in a yellow-green colouring. With solvents it was very hard to remove this colour.

A slight abrasion with sand paper gave the stone this original colour again.

As this is a very fast consolidation method, there is only a limited time to execute the operation. Indeed, once the DMA is added to the mixture monomer-BPO, the polymerization starts. In about 15' the impregnation must then be finished. There only then rests 15' to clean the apparatus.

3. Tests on consolidated samples.

3.1. Hardness.

Hardness tests give a very good idea of the improvement of the mechanical properties of the samples. The hardness was tested with a Clemen Hardness Tester, equipped with a Widia knife, loaded with a 1 kg weight. Table 3 give the average widths of the scratches.

g polym/g stone	width of the scratch in mm	improvement %
0 (reference)	2,7	-
0.149	0.49	82
0.176	0.38	87
0.223	0.43	84
0.142 (BPO)	0.63	76

Table 3 : Hardness tests on treated samples

As can be seen, the improvement obtained with the AIBN polymerization varies from 82 to 87 %. The BPO polymerization gives an improvement of 76 %, probably due to the lower polymer concentration.

3.2. Porosity.

Porosity also gives a good idea of the changes in properties. Porosities were calculated from the weight difference before and after saturation of the samples with water. For the thermal polymerizations, an improvement of 85 % was obtained, for the BPO-polymerization, the improvement was 66 %.

4. Conclusion

From the described experiments follows that tuff can be consolidated in an easy and cheap way. Only a simple apparatus is necessary for the impregnation and the polymerization. With the monomer mixture methyl methacrylate ethyl acrylate (50/50), initiated with 0.5 mol % AIBN, the polymerization will be carried out at a temperature of at least 65°C. Under these conditions, no risk of cracks will occur during the reaction. Consolidations at room temperature with the same monomer mixture but an other initiator give results which are less satisfactory. Experiments to improve the experimental conditions are under investigation.

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ETUDE D'UN PROTECTIF SUPERFICIEL
POUR DES MATERIAUX PIERREUX

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5ème Réunion triennale
Zagreb, 1978

ETUDE D'UN PROTECTIF SUPERFICIEL POUR DES MATERIAUX
PIERREUX

Guido Biscontin et Pavan Renzo

Resume -

On a pris en examen, en cette recherche, un protectif su
perficiel pour des marbres et des pierres non poreuses.
Le produit a été formulé après maintes épreuves de con_
frontation tout en tenant compte des exigences particu_
lières du secteur d'utilisation.

Le choix dut enfin porté sur des résines de nature acry
lique, lesquelles ont été additivées à des composants
qui en exaltent les caractéristiques.

De différents échantillons de marbres et de pierre trai_
tés on été placés en plein air pour bien 6 ans; ils ont
présenté, au contrôle, de bonnes propriétés protectives.
On a effectué également et parallèlement d'autres épreu_
ves de laboratoire, ce pour définir sur le produit les
propriétés chimiques et physiques qui le composent et
évaluer par-là, par des systèmes de vieillissement sa va_
lidité dans les temps.

Introduction -

On a pris en considération, en cette étude, la possibilité d'intervention pour la conservation des matériaux piereux moyennant l'utilisation d' un protectif superficiel. Ce type d'intervention conservatif commence à être de grand usage, soit en la protection des monuments en piere, soit en domaine du génie civil.

Poussés par cette exigence de créer une protection externe contre les effets de la pollution, nous avons cherché de formuler un produit dont les caractéristiques sont technologiquement bien définies.

On a bien tenu compte dans les épreuves de travaux pratiques soit de la condition particulière esthétique soit des propriétés techniques voulues. (1)

Après avoir examiné des différents types de résines de différente nature chimique, notre attention s'est arrêtée sur quelques résines du type acrylique (mélange d'esters d'acide métacrylique).

Nous pourrions observer ici au fur et à mesure toutes les épreuves effectuées pour vérifier l'efficacité de ce produit nouveau.

L'utilisation d'un protectif superficiel varie suivant les conditions du substrat que l'on veut traiter.

En général quand la pierre est de nature cristalline (marbres) et la surface se présente assez saine, le protectif peut être appliqué directement. Si, au contraire, le matériau à traiter est de nature poreuse (grès ou calcaire, etc) et la surface est fortement altérée par la dégradation, il est conseillé de consolider, au préalable, la pierre, moyennant des consolidants appropriés et enfin intervenir pour la protection superficielle. (2)

Un protectif peut être défini comme substance qui a pour fonction de protéger la pierre des effets de la pollution et des agents atmosphériques.

On crée de cette manière, naturellement, une surface (une pellicule) qui peut être renouvelée ou substituée périodiquement.

Une des propriétés fondamentales est la durée, pour que la manutention si même nécessaire, soit réduite au minimum.

Caracteristiques -

Quelles sont donc les propriétés d'un tel produit? (3)
Il doit donner, d'abord, une pellicule parfaitement tran
sparente, incolore, réversible, élastique, transpirable,
résistante aux cycles thermiques, hydrofugeante et natu
rellement stable soit aux agents chimiques de la pollu
tion soit aux radiations lumineuses.

On a pris en considération, dès le début, pour formuler
ce produit, des résines de différentes natures et puis
après maintes épreuves comparatives on a été porté vers
des types de résines acryliques thermoplastiques.

On a ajouté aux résines pures des différents additifs
pour en augmenter les caractéristiques de plasticité et
d'imperméabilité.

En ce qui concerne l'aspect, étant donné que les résines
donnent une pellicule brillante, on a ajouté des opacisants.
Voyons maintenant en particulier les enquêtes pour les
quelles le produit a été mis en examen.

Le produit formulé au 30% de sec en solvant donne une so
lution à viscosité Brookfield, barre 4 vitesse 20, de 1500
+ 2000 cps à 20°C qui s'abaisse remarquablement par aug
mentation de la dilution.

On a d'abord pratiqué des épreuves pour identifier le pro
duit en ses caractéristiques en tant que tel, et, parallé
lement d'autres épreuves portant sur des échantillons de
marbre et de pierre. Les éprouvettes sont restées à l'ex
térieur pour bien 6 ans et contrôlées périodiquement.

Resistance aux Rayons U.V. -

Cette épreuve est nécessaire pour vérifier la stabilité
de la résine aux conditions externes. Elle a été effectuée
en une chambre moyennant des lampes lignaires au quartz de
500 Watt, à la température de 30-35°C et une humidité con
stante.

Les éprouvettes sont de deux types:

- a) Feuille de verre sur laquelle on a éparé une pellicule
de résine de 100 micron -
- b) Une série de tranches de marbre de Carrare brillant et
non, de pierre de l'Istrie et de pierre de Vicence, sur
lesquelles on a éparé une pellicule de résine de 100
micron.

Successivement, après la polymérisation de la résine, les
feuilles de verre et les tranches de marbre ont été couver
tes par moitié par une feuille d'aluminium (dans une con

frontation directe des variations éventuelles de couleurs advenues), et mises en chambre.

Les échantillons sont ensuite prélevés par temps croissants et contrôlés.

Les variations de couleurs ont été suivies moyennant des mesures spectrophotométriques en transmission pour les échantillons sur verre et en réflectance pour ceux sur pierre. Les résultats ont montré une variation de couleur en 24 heures d'irradiation assez contenue.

Des observations à l'oeil nu ne consentent pas d'évaluer un jaunissement de la surface.

On a par contre vérifié qu'après des temps longs (100 h) d'exposition aux rayons U.V., la pellicule avait une certaine tendance à diminuer ses caractéristiques hydrofugeantes. Ce phénomène a été évincé par les mesures de l'angle de contact qui montraient des valeurs légèrement décroissantes pour temps croissants à l'exposition.

Des mesures d'absorption d'eau en ces conditions, n'ont pas donné pourtant, des résultats différents de ceux qui ont été obtenus avec les échantillons qui n'ont pas été placés aux rayons U.V. (fig.1 et 2)

Ce nous donne à penser que la pellicule maintient son imperméabilité.

Du diagramme (fig.1) les absorptions ont été exécutées sur pierre de Vicence, on pourra remarquer la faible variation due aux rayons U.V.

Cycles Thermiques -

Les matériaux pierreux ressentent souvent des phénomènes d'altération dus aux changements thermiques très brusques. Le plus caractéristique de ces changements est le gel et le dégel de l'eau présent dans les matériaux.

En ce cas l'effet de la résine est de ne pas laisser entrer l'eau dans la pierre (en évitant ainsi le phénomène de gélivité).

D'autre part la pellicule doit être de nature élastique pour pouvoir supporter les variations de volume des matériaux soumis aux cycles thermiques.

Pour bien vérifier ces propriétés on a soumis une série d'échantillons (des cubes de 3 cm. de côté) des matériaux sus-cités à des cycles de gel-dégel.

Un cycle est ainsi composé:

- 16 h à la température de -20°C humidité 80% et 8 h en H_2O distillée à température de 20°C .

Etant donnée la nature différente des échantillons traités,

il est nécessaire poser trois cas:

- Les échantillons traités de pierre de Vicence n'ont pas montré des signes d'altération après 70 cycles, tandis que le matériel non traité donne déjà à partir de 17 cycles des signes de fracture, très évidents.
- Sur les échantillons de marbre et de pierre de l'Istrie on a exécuté 150 cycles sans que l'on puisse constater un phénomène d'altération.

Des contrôles pendant les épreuves ont montré une marche assez constante d'absorption d'eau.

Réversibilité -

Cette propriété est particulièrement importante puisqu'elle nous donne la possibilité de remouvoir en tous moments le protectif, moyennant l'utilisation d'un solvant approprié.

Sur les échantillons traités et exposés extérieurement pour 6 ans, on a exécuté des épreuves de réversibilité. Moyennant un torchon de coton imbu de solvant en essuiera la surface traitée et l'on obtiendra ainsi tout de suite une destitution de la résine. La pierre soumise ne présentera aucune variation visible à l'oeil.

Résistance aux agents atmosphériques -

Des épreuves moyennant des échantillons (marbre et pierre de l'Istrie) ont été exécutées à l'extérieur à différents grades de pollution et ont montré une bonne résistance du protectif.

En effet, après la période (6 ans) d'exposition, la surface maintient encore ses caractéristiques, en particulier en ce qui concerne son imperméabilité.

Des épreuves en ce sens ont démontré que l'absorption de H_2O demeure toujours à des valeurs très basses, pratiquement nulles. D'autre part il est à remarquer que l'absorption d'eau est la cause majeure de l'altération des matériaux pierreux.

Au laboratoire même, on a exécuté sur des échantillons traités des épreuves de simulation d'ambiants polluants en une chambre, à l'humidité constante (80%) avec une atmosphère d'air contenant SO_2 , maintenu aux valeurs constantes de 100 ppm.(4)

La température de la chambre était maintenue constante à 20°C.

Le contrôle des échantillons effectué à temps croissants

de 1 à 360 heures, moyennant l'utilisation du microscope électronique à grands écarts, a montré une pellicule qui maintient assez bien toutes ses propriétés. C'est seulement vers les 300 heures que l'on commence à entrevoir les abords de vieillissement du matériel.

Hydrofugeage -

Il va sans dire que l'eau pénétrante dans la pierre est bien la cause majeure de la dégradation du matériel, soit parce qu'elle transporte des acides et des sels en solution qui puissent attaquer la pierre, soit parce qu'avec l'abaissement de la température peut geler intérieurement, augmentant ainsi son volume jusqu'à provoquer des lézardures et des clivages.

L'épreuve qui permet d'évaluer l'hydrophobie à l'eau du matériel, est affectuée moyennant l'extension d'une pellicule sur laquelle on pose une goutte d'eau. Cette dernière prend alors une forme sphérique qui tend à ne point mouiller la superficie traitée.

De cette exemple, nous pouvons dire que toute pluie ou eau en général ne réussissent pas à pénétrer dans le matériel; bien mieux, elles glissent sur la surface, rendant cette dernière bien sèche.

Il est bien clair que des pierres ainsi traitées pourront être facilement lavables par des jets d'eau, sans que l'on porte des dommages au matériel.

On pourra voir en fig.1 et 2, l'illustration de l'absorption de H_2O de la pierre de Vicence en fonction du temps; il est même possible remarquer le fort abaissement du phénomène.

Resistance aux agents chimiques -

L'épreuve consiste dans le fait de faire couler goutte à goutte la solution de l'agressif sur deux plaques inclinées à 45° en rapport à la verticale.

Les agressifs chimiques utilisés sont:

- | | |
|------------------------------|-------------------------|
| a) une solution de H_2SO_4 | 4% (acide sulfurique) |
| b) une solution de HCl | 4% (acide chloridrique) |
| c) une solution de HNO_3 | 4% (acide nitrique) |
| d) une solution de H_3PO_4 | 4% (acide phosphorique) |
| e) une solution de $NaOH$ | 4% (Hydrate de sodium) |

Le quantitatif utilisé du produit a été de 3 litres avec une vitesse moyenne d'écoulement de 50-60 gouttes à la mi

nute, pour bien 12-14 heures.

La pierre supérieure est celle qui a été traitée; la différence entre les échantillons est remarquable.

En général, la pellicule du produit a démontré une forte stabilité aux agents chimiques.

Les solutions ont été choisies arbitrairement ainsi que le temps d'écoulement des gouttes. Il va sans dire que toutes oeuvres d'art placées à l'extérieur subisse une agression de par les acides formés par la combustion des produits du pétrole.

D'autre part, les échantillons que nous avons exposés à l'extérieur, n'ont point montré de signes évidents d'attaque chimique.

On a effectué également des épreuves d'adhésion et de transpirabilité; pour la première par humidostatique à 45°C à 100% d'humidité relative pour bien voir la possibilité de détachement des pellicules favorisées par la vapeur d'eau. C'est après 240 heures que l'on a pu constater qu'il n'y avait aucune altération de la pellicule.

Pour la transpirabilité l'épreuve a donné des résultats positifs.

Conclusion -

Un revêtement de ce type représente une protection contre les agressions de l'environnement sans le moindre dommage. Il offre, en outre, la possibilité d'être enlevé en tous moments sans aucun inconvénient.

La durée du produit dépend soit du type soit de l'état de dégradation de la pierre, soit également de l'ambiant dans lequel se trouve l'oeuvre ainsi que de la technique d'application.

Ce type de produit formulé, il y a 6 ans, et appliqué à l'extérieur, soit en des zones industrialisées ayant des ambients fortement pollués (Milan), soit en des zones aux climats particulièrement froids d'hiver et très chauds l'été (La Région de Trente), montre bien sa validation. (4) (5) (6).

En outre des épreuves ont été effectuées en laboratoire et ont laissé prévoir une durée supérieure et qui pourra certainement être confirmé par le temps.

D'autre part il est évident qu'après un traitement, une maintenance rigoureuse est bien nécessaire sans laquelle on limite fortement l'action préventive et protectrice de n'importe quel produit.

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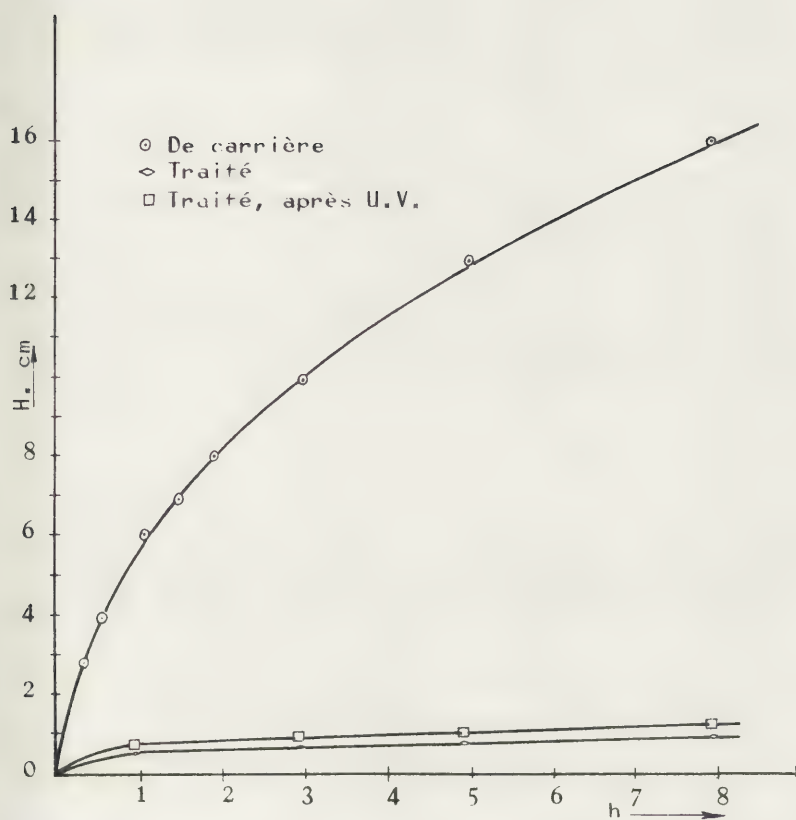


Fig. 1 Absorption d'eau de la pierre de Vicence par ascension capillaire.

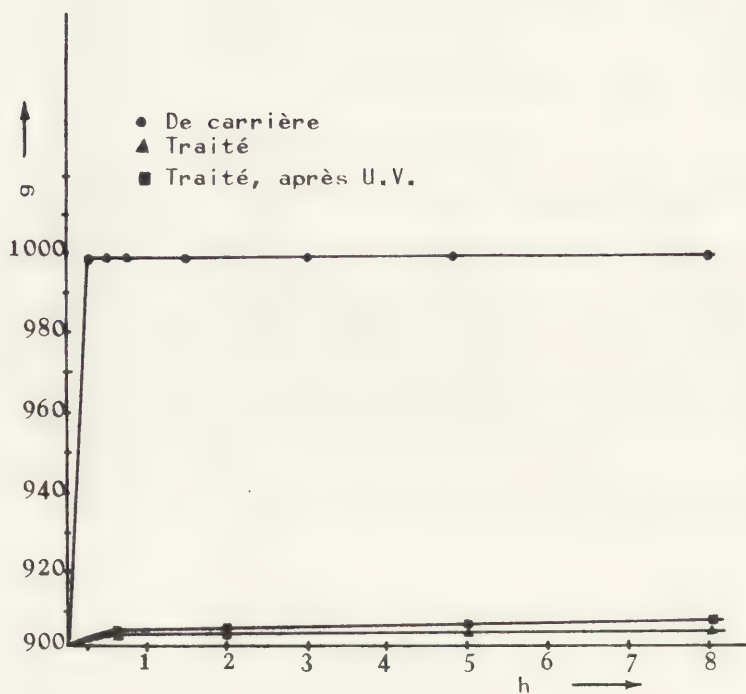


Fig. 2 Absorption d'eau de la pierre de Vicence par immersion.

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LA RESTAURATION DES STATUES GOTHIQUES
RENDUES AU JOUR AU CHATEAU DE BUDA
(HONGRIE) EN 1974

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LA RESTAURATION DES STATUES GOTHIQUES RENDUES AU JOUR AU CHATEAU DE BUDA (HONGRIE) EN 1974

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Extrait. La trouvaille des statues extrêmement riche rendue au jour au château de Buda en 1974 signifiait une tâche hors ligne pour la restauration de la sculpture de pierre de Hongrie. Il se profilait des grands nombres des fragments de la culture plastique du cour royal de Buda du 14^{ème} siècle. Notre effort tendait à présenter dans la mesure de possible la complète trouvaille à l'exposition du Musée Historique de Budapest, faisant voir la richesse de la trouvaille. Nous devions composer de la matière fragmentaire des unités raisonnables, sans cela, que nous rendions plus difficile les examinations scientifiques suivantes avec des complètement excessifs, par travaillant ensemble de définitions.

Nous avons utilisé les principes suivants au cours des travaux de restauration:

1./ Les fragments ne doivent pas être endommager par les circonstances de stockage.

2./ Les surfaces de pierre ne doivent pas être détériorées durant le nettoyage.

3./ On doit travailler ensemble seulement ça, qui appartient ensemble démontrablement.

4./ Le complètement des manques doit être fait que dans les cas les plus nécessaires.

5./ Les compositions ne sont pas à compléter avec la reconstruction des parties manquantes.

6./ Les matériaux supplétifs doivent être distinguables du matériel de pierre original.

7./ Les goujon à incorporer doivent être construits du matériel anticorrosif.

8./ La retouche statuaire et picturale doit être de minimum.

9./ L'affermissement du matériel de pierre et la conservation des restes de peinture ne doivent pas causer une altération visible.

10./ Il n'est pas permis d'incorporer des goujons définitivement dans les surfaces de cassures sans continuation.

11./ On doit faire valoir en mesure complète les méthodes modernes des examinations de sections.

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12./ Les sculptures, qui ne sont pas exposées doivent être placées dans un dépôt d'études.

13./ On doit élaborer une documentation du travail de restauration.

/Je vais illustrer ma lecture avec 39 plaques diapositives./

Au cours des fouilles exécutées au territoire du château de Buda Béla ZOLNAY archéologue a apporté au jour en janvier et février de 1974 au voisinage des bâtiments du 12ième-13ième siècle d'un niveau de 5 et demi mètres plus profond comme celui d'à présent, pendant la mise au jour d'une citerne ceinte des murs, une grande quantité de statue cassée et enterrée. A la base des trouvailles de médailles l'archéologue a daté l'enterrement des statues entre les années 1430-40.

Depuis le 21ième février 1974 j'ai visité systématiquement les fouilles, j'ai observé les circonstances de trouvaille des fragments de statue, j'ai pris part dans le rendement au jour des trouvailles. Nous avons placé les trouvailles sans nettoyage dans le dépôt voisin de l'atelier de restauration du musée.

J'ai reçu la charge de restaurer la trouvaille de statue. Regardant le grand intérêt, notre ambition était de présenter la trouvaille le plus vite possible à notre public. Nous avons ouvert l'exposition au 4ième avril 1976 pour le public dans le Musée Historique de Budapest. Les investigations, l'adaptation et la restauration du matériaux placés dans le dépôt d'études se continuait.

Dans ma lecture actuelle je voudrais faire voir le volume du matériel découvert, la grandeur de la tâche de sauvetage, de la conservation, de l'adaptation, etc., et nos principes suivis pendant la réalisation de nos tâches. Le matériel fragmentaire figuré du cimetière de statue rendu au jour pendant les fouilles était étonnement riche. On a trouvé quasi trois milles fragments plus grands et petits, des torses et des têtes, la multitude de membres de corps et des détails de draperie, plus de cinquante détails de statue sculptées, dans un tas, avec quelques sculptures architecturales, des tuiles, des os et quelques objets, qui déterminent l'époque, dans des couches argileuses et terreuses, intactes et brûlées.

Il y avait quelques torses, qui ont reparu relativement dans l'unité. Par exemple le torse d'un chevalier ou d'un roi, avec à côté la partie du tronc d'une figure de femme, à ses pieds avec la partie supérieure d'une petite statue de Madonne, et le tronc supérieur d'une figure d'héraut barbu, tous sans tête.

Quelques torses sont parfaitement effrités, et nous pouvions constater, que la majorité d'eux étaient cassés,

mutilés et incomplets avant de leurs enterrement, et on a les a enterrés dispersement.

Les fragments de sculpture souillée différemment étaient faites presque sans exception de pierre calcaire tendre. Pour éviter leurs détérioration ultérieure nous les avons placées sur des plaques de matière plastique, puis sur plaques de mousse spongieuses.

Notre première tâche était le nettoyage conforme aux exigences. Ça signifiait une si grande tâche que les restaurateurs du Musée Historique de Budapest devaient pour un long délai mettre à côté tout autre travail. Dans le cas d'une figure de héraut sur le pied gauche se montrait une tache petite, claire, c'est-à-dire la couleur originelle de la pierre poreuse et absorbante. Nous devions d'abord appliquer un nettoyage mécanique, parce que avec un lavage quelconque nous aurions fait entrer les contaminations dans la pierre. Cette même sculpture est devenue appropriée après le nettoyage, que cherchant les parties y appartenant on puisse mettre ensemble les parties, qui appartenait jadis ensemble.

Il s'est vite dévoilé pendant la sélection qu'il y en a beaucoup de sculptures solitaires, comme par exemple la tête d'homme au chapeau, on trouve des torsos sans têtes, et des parties de draperies sans figures.

Une sainte petite, de 80 cms manquait que la tête et la main gauche, et elle était ainsi la figure la plus parfaite de l'ensemble. La métacarpe de cette statue était déjà une partie appliquée. Ce n'était pas un symptôme isolé, nous avons observé la même chose avec plusieurs figures.

Suivant cela nous faisons effort pour marier tout les fragments des statues particulières cassées. De la petite statue de Madonne nous avons trouvé au corps supérieur mentionné déjà, une partie d'inférieure aussi. Ajustant les deux parties ensemble, il se formait déjà une figure concrète. La structure fine de son matériel de pierre, sa qualité artistique haute, ont de même aidé pour que nous pouvions identifier les autres fragments, qui jadis appartenait à cette statue. Comme les fragments particuliers ont changé de teinte ou après leurs enterrement, ou déjà en avant, les membres d'une unité n'étaient prouvées que par son matériel, par sa forme et par la surface de cassure. La petite statue de Madonne est devenue après une sélection précautionneuse relativement complète.

La draperie flottante de son bras gauche se composait de beaucoup d'éclats minuscules. Dommage que sa tête, ses mains et le petit Jésus manquent. Ce dernier n'est certifié que par les orteils rester dans la région du ventre. Sur cette figure nous avons point trouvé des traces

de peinture, ni avec transformateur d'image infrarouge, ni en lumière ultra-violette.

Nous pouvons dire la même chose d'une statue de chevalier presque de grandeur naturelle. Après le nettoyage nous avons travaillé ensemble les fragments bien assortis, et avons laissé libre les manques, sans tout complètement, parce que le complètement aurait eu allé au détriment d'authenticité.

Une figure de femme avait été aussi exposer sans complètement. Un fragment de visage, comme il est a présumer, y appartient, mais sans connection directe. Dans des cas pareils nous avons rejeté la pensée de l'intégration. Pour coller nous avons utilisé de la résine synthétique avec catalyseur, toujours de façon, que les contours du cassement collé restent propre. Nous devons conserver les surfaces des cassements intact, car elles ont servi dans certains cas comme base des études suivantes. Par exemple sur l'un des fragments - qui est qualifiable d'après notre opinion comme tête d'étude - la rupture ne s'est pas produite au temps du jet, mais les contusions réduites en poussière si. Alors quand le fragment s'entrechoquait avec une autre sculpture de pierre. Ces tâches tendres, d'une structure molle nous avons raffermi avec la solution acétonique diluée de l'acétate de polyvinylevinavyl.

Pour la conservation des restes de peinture trouvées sur certain fragments nous avons utilisé un copolymère de matière première de méthylméthacrylate diluée en chloroform-toluène. Sur une jolie tête, après la mise au jour, devant le nettoyage, aussi pouvait on bien voir la peinture des pupilles des yeux. La sculpture était humide dans cet état. Après le nettoyage et la désiccation la peinture des yeux devenait pâle. La conservation de cette peinture rendait les pupilles de nouveau animées. La tête est probablement le portrait de jeunesse de Sigismond de Luxembourg, roi hongrois et empereur de l'Empire d'Orient. Malgré la finition détaillante elle est inachevée d'après le témoignage du bloc encadrant de l'oreille gauche.

Sur une autre tête de roi, qui n'est pas faite avec l'exigence d'un portrait, mais qui est une tête caractéristique "des trois Mages" pas seulement les pupilles étaient peintes, mais tout le visage aussi. La tête est probablement une étude, ou faite comme oeuvre d'examen dans l'atelier royal. Il faut l'estimer comme un oeuvre indépendant, et pas comme la tête d'une statue. Nous avons réussi de refaire des fragments passants ensemble aussi une figure vêtu d'une armure, vrai que sans sa tête, une partie de sa main droite, ses pieds et plaque de base. Chez cette figure refaite de 24 parties, et chez toutes les torsos avec des manques similaires, nous trouvons un problème spécial, que comment nous devri-

ions mettre debout la statue pendant notre travail, et aussi à l'exposition, parce que le mouvement de rotation de tourner les plastiques en position couchée n'était pas rassurant même avec les précautions les plus soignées. Dans des cas pareils nous avons préparé des plans schématiques, prise en considération les différentes possibilités de solution, et nous avons décidé de poser les torsos incomplets sur une substruction avec une surface négative de la surface de cassure. La solution définitive venait d'être faite avec des formes considérablement plus simple. Nous n'avions pas incorporé des goujons définitives nul part dans la partie inférieure de la surface de cassure des torsos. Chaque plastique sans plaque de base, ainsi par exemple la statue d'évêque ci-mentionnée, nous avons étayé par en dessous à trois points de façon, qu'elles soient debout statiquement, et qu'on peut les tourner avec une plaque tournante posée au-dessous dans toutes les directions, que nous pouvons accéder à la plastique librement de tout les cotés pendant les travaux de nettoyage et de coller ensemble.

Pour l'exposition on a préparé des piédestales de matière plastique transluide, colorée, avec surface polie, où toute la surface de cassure reçoit un chargement uniforme, en tenant la plastique en état de parfaite conservation, parce que de notre part la surface inférieure du cassement peut encore devenir importante. La plastique est toujours à enlever de son piédestal.

Nous avons étudié les proportions du corps en détail dans la relation de la hauteur de la tête, que nous puissions classer les fragments appartenants à les figures de différentes mesures. Nos torsos sont relatives à la toise de l'époque Anjou /à peu près 189,6 cms/ approximativement de grandeur naturelle de cinq-septieme, de quatre-septieme et de trois-septieme, et dans leurs proportions composées a sept longueur de tete.

Nous nous devons occuper avec les schèmes de mouvement des figures particulières aussi. Par exemple les lignes de mouvement d'une Madonne se continuent dans la tête, et définissent presque la tenue de celle. Quelques uns de nos collègues historiens d'art auraient vu volontiers si nos torsos auraient reçu des têtes.

Mais en vain a-t-on fait le corps de Madonne et la tête de Madonne du même matériel de pierre, en vain était l'échelle de proportion aussi bonne, correspondante, car ici des lignes de mouvements d'une direction inverse se heurtent et à cause de la dissonance se pré-sentante il n'était pas possible de former une figure.

Nous tous avons de l'affection pour voir des statues plus complètes au lieu des torsos. Mais s'il nous est réussi de constater que ça qu'une tête et un corps vont ensemble et la connexion détaillée n'est assurée

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que par l'identité du matériel, de l'époque, du style, de la pratique de l'atelier, alors nous avons exposé la tête et le torse séparément, documenté avec cela aussi que la formation d'une figure n'était pas possible.

Il faisait partie de notre travail de faire des études d'histoire de costumes de cette époque, et la recherche des analogies aussi. Nous devions étudier en détail les costumes, que nous reconnaissions nos fragments de cette point de vue aussi.

Par exemple pour la sélection des fragments d'une draperie d'une statue de chevalier nous avons trouvé très utile les dessins de coupe en familiarité avec les costumes, qui ont beaucoup mieux définie le système de draper les plis, comme les dessins de vue. Les contours de forme et leurs enchaînement logique dans les surfaces de cassure est clairement reconnaissable. Ils signifiaient un point d'appui ensuite par exemple dans ce cas les taches de peintures restées rouges sur les bas, bleu sur la tunique et sur la veste de cuir, ainsi que l'or luisant sur la bordure de la partie de robe. Ainsi le coloriage, comme l'or sont peintes directement à la surface de pierre. Avec ce travail minutieux il nous est réussi de réunir trente sept pièces.

Sur certains statues ecclésiastiques, comme par exemple chez la nommée Marie bleu la technique de peinture est de deux sortes. Le bleu azur de la mante était probablement peinte avec un agglomérat d'une solution aqueuse, le brun-rouge de la tunique et des cheveux est comme un tempéra à huile, qui est resté presque complètement.

Notre statue, qui est devenue la plus complète est une figure de prophète. A son corps de trois pièces nous pouvions ajouté dix neuf détails plus petits. Les trous de cassement perturbant on a radoucit avec du mortier à chaux et à sable. Les restes de peinture de couleur bleu sur les vêtements ne sont pas ici sur la surface de pierre, mais sont peintes sur une couche de fond de craie, comme c'était généralement le cas chez les statues de bois.

Nous avons rencontré le même système de peinture chez plusieurs statues. Par exemple chez une figure de prophète barbu ou d'apôtre aussi. Chez ces statues on a fait les métacarpes comme des pièces appliquées. Leur identification était fait possible par la coïncidence des goujons et des trous pour goujon. La métacarpe droite venait d'être découverte pas dans la voisinage de la statue, elle était parfaitement noir comme de la suie, dans l'intérêt de la harmonie des teintes de la composition nous avons lacé la main avec une solution d'eau oxygénée. Dans le travail de nettoyage c'était notre

plus forte intervention, que nous avons tenu nécessaire pour radoucir les différences disturbantes.

Nous avons complété chez une statue de héraut dans l'intérêt de la représentation une petite partie manquante au-dessus de la cheville du pied pour assurer l'unité de la composition avec du mortier à chaux et à plâtre avec écrasement de pierre de stabilité plus faible que la pierre. Ici on n'a pas fait d'autre complètement. Pour l'étayage à cause de remplacer la drapérie inférieure manquante nous avons intégré un bâton de cuivre d'une longueur de dix millimètres, qui est librement visible.

Nous pouvions seulement assurer la statique d'une statue d'un héraut tenant un casque, que nous avons étayé le corps supérieur avec la reconstruction partielle de la drapérie derrière le pied gauche. Nous avons reconstruit une partie de la casque, tenue dans la main, aussi que la relation de la partie supérieure et inférieure soit univoque aussi pour les gens inexpérimentés. Nous avons fait la même chose chez les trous de cassure larges de la jambe gauche.

Chez la statue la plus complète de chevalier nous ne pouvions pas rallier les bras présumés. Il manque une section du pied étant debout et du support d'arrière, et la stabilité est assurée des bâtons de cuivre intégrés. Appréciant les possibilités des formes de déplacement, ici nous avons aspiré à rendre la forme originelle, par l'addition de la section attachante qui manquait. Nous avons réalisé l'addition de la section de la jambe inférieure et du support d'arrière de façon, que l'addition doit être distinguable des parties originelles, ainsi démarquant ces limites aussi. Alors nous n'avons pas suivi un principe rigide en faisant nos additions, parce que la différence des plastiques particulières exige de diverses solutions.

Peut-être la pièce la plus importante dans l'appréciation de toutes les statues est la statue plusieurs fois mentionnée, de l'évêque inachevé et dégrossi. Son importance n'est pas assurée par ses qualités artistiques, mais par la chose qu'elle est une épreuve manifeste de la vie, des méthodes de travail et des traditions de l'atelier royal entre 1370 et 1440, parce que cette statue a été enterrée d'après les usages d'atelier du moyen-âge. Ici je ne pouvais faire connaître que quelques problèmes frappants.

On a préparé de tout le travail de restauration et des examinations des experts une documentation détaillée, qui contient au total un texte de 208 pages en format dactylo et 1274 photos.

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J'ai confiance en ça qu'il m'est réussi d'éveiller l'intérêt de vous avec cette étude présentée sur le travail de la restauration, regardant la trouvaille de statue du château de Buda, et beaucoup de vous vont chercher l'opportunité de faire connaissance avec cette groupe de statues, qui est intéressant de point de vue de restaurateur aussi.

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POLYVINYL ACETATES FOR THE PROTECTIVE
TREATMENT AND CONSERVATION OF HISTORICAL
OBJECTS OF STONE AND OTHER MATERIALS
(RESEARCH WORK AND EXAMPLES OF
APPLICATION)

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978



POLYVINYL ACETATES FOR THE PROTECTIVE TREATMENT AND CONSERVATION OF HISTORICAL OBJECTS OF STONE AND OTHER MATERIALS (RESEARCH WORK AND EXAMPLES OF APPLICATION)

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Abstract - The aim of laboratory investigations was the synthesis of polyvinyl acetates specially intended for the conservation and protective coating of historical objects made of stone and other materials. Polyvinyl acetates were used as preservatives for test samples of the materials collected from historical objects, which were next exposed to rough atmospheric conditions. Important examples of the treatment and the effects of the conservation work accomplished are presented.

Preparation of a Protective Polymer and Programme of Laboratory Research

The aim of the present experiments was to obtain a synthetic macromolecular substance that would effectively protect the building and artistic materials of historical objects, damaged by various factors. Investigations were carried out on samples of definite size and shape which had been collected from decayed authentic historical objects; these samples included stone, brick, plaster, porcelain and faience, wood, bone, and even binders of oil paintings.

Analyses of a dozen or so kinds of synthetic plastic demonstrated certain sorts of purified polyvinyl acetates obtained by special procedure to possess the largest number of the properties rendering them suitable for the conservation and protective coating of the above-mentioned materials /11,12,22/.

In order to ensure the broadest possible range of the properties of the polymer of vinyl acetate and thereby its many-sided application to conservation of historical objects made of different materials, it appeared indispensable to achieve a high degree of purity of the monomer by removing from it the synthesis and decomposition products and in this way obtaining the acetic acid content of about 0.027 % and that of acetic aldehyde of about 0.032 %. As a result of such a considerable reduction of the two impurities the monomer became enriched to the so far highest recorded vinyl acetate content, i.e. to 98.90 - 99.28 %. These achievements made possible the regulation of the controlled polymerization process. Thus, polyreaction in methanol yielded polyvinyl acetates of facultatively programmed molecular weights ranging from about 70,000 to about 500,000, and even rising to 700,000 /7,22,23/.

Furthermore, owing to the rectification of polyvinyl acetate solutions so obtained, one of the essential problems was solved regarding the permanent lack of colour of the rectified products and of the foils obtained from them /1,2,7,8,9/.

The only substances employed in the present author's research work and in conservation practice were solutions of polyvinyl acetates in methanol of a high degree of purity. They were used for soaking or coating of appropriate surfaces of the samples studied or the materials of historical objects to be protected. The areas to which the polymer solutions of definite concentration were applied, revealed the formation of highly adhesive colourless films /2,22/. Therefore, the present authors have undertaken some basic studies /4,7,22/ on the properties of the protective foils obtained with some varieties of one kind of polyvinyl acetate.

The general assumptions determining the required properties of polyvinyl acetate and the directions of researches on these problems made by the present investigators were as follows:

1. Mutual chemical passivity of the protective foils and the coated material /11/,
2. High and permanent adhesion of the foil to the material protected /3,21,23/,
3. Proper mechanical strengthening of the coated material /17-20/,
4. Resistance to the action of corrosive gases: H_2S , SO_2 , Cl_2 , and HF and CO_2 with water vapour /11,22/,
5. Resistance to rough natural atmospheric conditions: sunlight, thermic effects brought about by insolation, and to water and water vapour /10,12/,
6. Stable lack of colour, and transparency /7,19/,
7. Maximum resistance to ageing process /13/,
8. Proper, two-way exchange of water through the foil coating the object /17,18,23/,
9. Capacity to stabilize processes of destruction of materials, evoked by insects, bacteria and moulds /4,6,7/.

Extensive, many years' studies have given positive answers to all above-itemized conditions required of protective and binding foils.

The results of researches and experiments and the problems of conservation presented here in outline, are described in detail in the author's unpublished, comprehensive study / 7 /.

Examples of Conservation Work

The results of laboratory examinations and the treatment given to the elements of old buildings and a variety of historical objects justified the application of polyvinyl acetates to conservation, protective coating and reconstruction of such objects, even those representing the highest cultural values. The work was done by conservators /14/.

1. Stone. Among the first examples of the efforts made in 1958 to protect and reconstruct glauconite sandstone was the impregnation of the architectural elements of the elevation of the Wawel Castle with a c. 3.5 % methanol solution of polyvinyl acetate. Damaged by a continuous action of water, the sandstone had a number of erosions 1.5 - 4.5 mm deep over the area of c. 2 m². After the stone had been cleared of mould and cleaned and after it had dried, it was impregnated with a solution of the polymer with the 485,000 molecular weight. Following impregnation, the areas of considerable losses up to 45.0 mm in depth and c. 130.0 mm in diameter were filled with glauconite sandstone in the form of a mixture of flour and crushed gravel with addition of a 5 % methanol solution of the polyvinyl acetate which was used for impregnation of the element.

Despite the lapse of 20 years from the time of the treatment carried out by Prof. Rudolf Kozłowski, Chief Conservator of historic objects on Wawel Hill, the thus protected element, while being fully exposed up to now to atmospheric factors, has been found to undergo no perceptible changes in its structure or chemical composition. This was also Prof. Kozłowski's opinion, and he gave it to R.J. Biliński with the following final statement, "Until now no unfavourable changes have been observed. May 30th, 1974". Therefore, as stated above, the corrosion of the stone had been effectively stopped. On the other hand, it has been observed that a small portion of the stone surface which remained unimpregnated on purpose, has undergone clearly perceptible deterioration.

The description and photographic documentation of the procedure can be found in the Archives of the Wawel Castle.

2. In 1959 the polyvinyl acetate which had been used for protective coating and reconstruction of the architectural element of glauconite was applied to impregnate the external /Berrecci/ portal on Wawel Hill, carved of Dobczyce sandstone. The aim of the treatment was to stop the process of corrosion /damp patches, mould/ and to protect the object from new attacks of these damaging factors. Impregnation was carried out with 1% and 3% methanol solutions of polyvinyl acetate. Prior to and following the treatment photographic documentation was prepared, which is now available in the Archives of the Wawel Castle. As described in the protocol, the progressing corrosive process caused by damp patches and the development of mould became stabilized.

3. Sixteen years ago some interesting studies were conducted in the conservator's workshops on Wawel Hill as tests preceding realization in stonework, polyvinyl acetate being used as a preservative. Tests for the durability and efficiency of the protection and reconstruction with an appropriate polyvinyl acetate were performed on a

block of deeply corroded glauconite sandstone - an element of Baroque masonry from Wawel Hill. The sandstone was repeatedly impregnated with a 1% methanol solution of polyvinyl acetate of the 485,000 molecular weight and fillings were applied to it of artificial sandstone made of a mixture of glauconite flour and crushed grit bound with the same polymer. Besides, fillers of another kind of sandstone and of artificial brick were used. The present condition of the thus treated stone conforms in the tiniest detail to the photographic documentation prepared 16 years ago. Several conservators have made use of this experiment in their own work.

4. In 1972, among a number of conservation tasks were the protective treatment and partial reconstruction of the stone in the historic parish church at Szydłowiec /Radom Voivodeship/, dating from the turn of the 15th and 16th century. While treating the masonry of the church, 5 - 8% methanol solutions of polyvinyl acetate with the molecular weight of c. 324,000 were applied. It was necessary to secure on the presbytery vaulting and to join together the ribs of Szydłowiec sandstone which framed the picture of Our Lady and which, owing to partial corrosion and other factors, were in danger of falling off. Furthermore, protective procedure, conservation, and a certain amount of reconstruction were performed on the rood-arch executed in the same kind of sandstone. The walls and rib elements were impregnated with 2 - 3.5% solutions of the same polymer. The joining of the ribs and replacing in them of lacking parts was accomplished with the putty of sandstone flour and 8 - 10% solutions of polyvinyl acetate. Up to now, after the nearly six-year period no unfavourable changes have been observed in the state of the treated objects.

Plaster. In order to protect, reconstruct and preserve the plaster which had become damaged, delaminated and torn off the substratum, the following substances were used, depending on the location of plaster: 1 - 5% solutions of polyvinyl acetates with the molecular weight of c. 200,000 for inner walls, whereas the plaster exposed to extremely severe effects of atmospheric agents and fate /walls and façades/ was treated with solutions of the polymers whose molecular weights ranged between c. 300,000 and c. 450,000 or even 600,000, similar to those applied to the protection of stone materials exposed to drastic atmospheric conditions /7, 19 /.

1. For over 20 years a number of conservators have been using polyvinyl acetates to protect various kinds of plaster. Worthy of note is the parish church at Świebodzice-Pełcznica /Wałbrzych Voivodeship/ owing to the character and extent of destruction and to the value of the amassed photographic documentation. Particularly badly damaged were the outer walls of the southern gallees

added at the turn of the 15th and 16th century. Big interstices and smaller cracks in the wall and plaster losses brought about by the water of the substratum and by rainfall and snowfall had caused damage to the outer walls and to the inner walls with polychromy. For the entire conservation procedure polyvinyl acetate with the molecular weight of c. 400,000 was used. The applied putty consisted of stone flour with addition of a 12 - 15% solution of the polymer. Here and there apertures were left on the plaster hardened with 2% to 8% polyvinyl acetate solutions and these apertures were next filled with the putty which joined particular patches of plaster. This interesting technology was worked out and employed in 1969.

2. Between 1965 and 1975 protective treatment and reconstruction of various kinds of plaster as well as conservation of mural paintings were carried out in several places. Protective coating and conservation were done, using polyvinyl acetates, in some monumental structures - churches and castles - among them in the rooms of the castle at Zator near Oświęcim. In 1960 the present authors were commissioned with the elaboration of the methods and means of protecting and reconstruction of stucco-work and plaster. The polymers used for the conservation of plaster on inner walls had molecular weights of c. 200,000.

3. In 1965-1975 polyvinyl acetates with molecular weights of c. 200,000 were applied to protect plaster and to preserve mural paintings in some 15th and 16th century houses in Cracow, i.e. in those in Floriańska St., Szczepańska St., in Mały Rynek /The Little Market/, and in other parts of the city. On the other hand, the elevations of these buildings were treated with polyvinyl acetates of predominant molecular weights of c. 400,000, or more, in special cases. Apart from the above-described objects, polyvinyl acetates were employed to protect numerous monumental structures and old houses in Olsztyn, Tarnów /the townhall/, and other towns.

4. Particular attention deserve the present authors' efforts to protect and preserve the ruined plaster and mural paintings on the façades of the courtyard and the outer walls of the castle at Baranów Sandomierski. The poor state of the plaster was caused by an exceptionally intense corrosive action of industrial gases; the mixtures of gases were SO_2 , H_2S , and HF with water vapour. Polyvinyl acetates used for protective and conservation treatment were identical with those applied to stone materials; besides, special modified polyvinyl acetates were employed / 7 /. While selecting appropriate polyvinyl acetates for protective treatment of stone and plaster, indications of scientific and professional literature were followed /10, 19 /.

Wood. Out of a great number of wooden historic buildings and their elements and of movable objects of historical value, which had been treated with polyvinyl acetates during protective coating, conservation and reconstruction, only a few are mentioned below.

1. In 1955 protective coating was applied to plain and polychromed authentic Renaissance ceiling beams in the royal chambers of the Wawel Castle /documentation in the library of the Board for Restoration of the Wawel Royal Castle/.

The beams to be protected and preserved, and also reconstructed, were in a very poor condition. Some parts were almost completely eaten by anobium striatum and other wood-boring insects. The beams rescued in 85 % were subjected to hardening by means of soaking with 2.5 - 5.0 % methanol solutions of polyvinyl acetate, thereby also the insects being killed, as in this case the polymer foil has stabilizing properties as well /7, 22 /. The obtained polymer had the molecular weight of c. 170,000 and was not as yet colourless. The impregnated beams were joined in various ways and were glued with a 20% solution of the polymer. Today, after 22 years have passed since the treatment, the beams are in the excellent state of preservation/7/.

2. The church at Sękowa /Krosno Voivodeship/, one of the oldest monuments of Polish wooden architecture /c.1520/, was subjected to conservation and protective treatment in 1960. The processes were carried out on the church walls of solid construction and on the pulpit and stalls. The molecular weights of the polyvinyl acetates employed were c. 150,000 and c. 180,000. The 1966 and 1974 inspections of the state of preservation of the object showed it to be exactly the same as in the year it was treated.

3. In 1961 similar problems and methods of treatment were dealt with in the church at Krużlowa /Krosno Voivodeship/ and in the church of the Poor Clares in Nowy Sącz, with very good results. Treatment was given to the elements of the wooden choir and stalls /13th and 14th centuries/ worm-eaten in nearly 90% by anobium striatum. They were hardened and fillings were made of wood flour and methanol solutions of polyvinyl acetate of the molecular weight approximating 180,000. The state of the objects has remained unchanged to this day.

4. A 15th century triptych in the Wawel Cathedral, precious for the Polish culture, presents an extremely interesting case in terms of conservation work. It was subjected to treatment in 1958 /by Prof. R.Kozłowski/. The entire panel of the bas-relief, worm-eaten by anobium, was as soft as a sponge. The present state of the triptych clearly testifies to the excellent effect of all three

conservation procedures applied, i.e. protective treatment, conservation, and reconstruction. Hardened with polyvinyl acetate of the molecular weight of c. 350,000 /3 - 8% methanol solution/ and subjected to conservation 20 years ago, it is in a perfect state now.

Porcelain, faience, bone. 1. That polyvinyl acetates are not only of great and many-sided applicability to building materials but can also be used for treatment of artistic materials is exemplified by a 17th century Chinese vase of hard porcelain, which was glued and reconstructed in 1960 /its dimensions: c. 120 cm in height, c. 68 cm in diameter, and 2 - 2.7 cm in wall thickness/. It had been broken to more than twenty pieces. Fairly remarkable is the result of measurements of the strength of adhesion between two surfaces of the fracture of hard porcelain, which amounts to 70 - 82 kg/cm² for the polyvinyl acetate binder of the molecular weight of c. 500,000.

2. A similar example, of slightly larger dimensions, is provided by an 18th century Japanese porcelain vase.

3. The analyses have shown that the bone head of a crozier, which in 1961 was given protective treatment with polyvinyl acetate of the 240,000 molecular weight, has till now remained in the state which does not give rise to any reservations.

Likewise, all other so protected historical objects of porcelain, faience, bone, and other artistic materials have suffered no changes for over a dozen years.

The research work and the employment of the prepared polyvinyl acetates to protective coating and to other conservation procedures have demonstrated a wide range of possibilities of their application. Apart from a number of essential positive protective properties, the fact that polyvinyl acetate is permanently colourless and resistant to destruction by oxygen, ultraviolet, and living biological agents testifies to its very high qualities. It should also be emphasized that all hitherto conducted optical examinations and detailed observations of the objects coated have proved that their surfaces do not suffer the slightest disadvantageous effect of the application of polyvinyl acetate foils /7, 14, 19/. The optical analyses of the surfaces and deeper layers of the impregnated objects of stone and other materials have pointed to only negligible variations in reflectometric determinations, amounting to 1 - c. 2.5 % as compared with the results of the determinations of the reflection of the surfaces of the materials which were not coated with a foil of polyvinyl acetate. The appearance of the coated stone and other materials remains absolutely true to their specific texture and to the artistic expression of an authentic object.

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CHANGES OF LIMESTONE PROPERTIES AS A
RESULT OF TREATMENT WITH POLYBUTYL
METHACRYLATE AND COPOLYMER BMK-5

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5th Triennial Meeting
Zagreb, 1978



CHANGES OF LIMESTONE PROPERTIES AS A RESULT OF TREATMENT
WITH POLYBUTYL METHACRYLATE AND COPOLYMER BMK-5

E.N. Ageeva, N.G. Gerassimova, M.N. Lebel and
E.P. Mel'nikova

Abstract

Some experimental results of the effectiveness of the impregnation of limestone with polybutyl methacrylate of low viscosity grade (PBMA) and copolymer BMK-5 by means of "suction" technique are given. The treatment with PBMA xylene solutions followed by retarded drying is shown to give a deeper penetration and a more uniform distribution of the polymer in comparison to similar treatment with PBMA solutions in mixtures of xylene and ethanol (1:1) and white spirit and xylene (9:1). The treatment with PBMA increases the stability of the limestone. BMK-5 in solvent mixtures penetrates into the limestone at the depth of not more than 3 mm and does not strengthen it. The experimental evaluation of polymer distribution in the sample is suggested. This is done by comparing the waterabsorption of the plates obtained by cutting the samples after treatment with the initial waterabsorption of the sample.

Polybutyl methacrylate of low viscosity grade (PBMA) has been applied at the State Hermitage for the restoration of limestone works of art since the early 50s. By brush impregnation with PBMA xylene solutions, by emerging or

by the "suction" technique the destroyed limestone of a number of Ancient Egyptian or antique monuments were successfully consolidated /1,2/. But we think that the problem concerning the changes of the limestone properties and of the distribution of the polymer has not been sufficiently studied. W. Domaslowsky and J. Lehmann /3/ after treating the limestone with polybutyl methacrylate solutions in various solvents^{*} found that white spirit gives the most uniform distribution inside the stone, while solutions in acetone, benzene, toluene, xylene and some other solvents give only peripheral distribution of the polymer. This, in the authors opinion, is to be accounted for by the pulling up of the polymer to the surface in the course of drying.

In our work the effectiveness of the limestone treatment was studied. The treatment was carried out by the "suction" technique, with PBMA solutions in xylene, in the mixtures of xylene and ethanol (volume ratio 1:1) and white spirit and xylene (9:1), as well as with BMK-5 solutions in mixtures ethyl acetate-acetone-xylene (1:1:2) and butyl acetate-ethanol-butanol-toluene (5:1:2:2). The specific viscosity of 1% PBMA solution in acetone was 0,27, BMK-5 (the copolymer of butyl methacrylate with 5% of methacrylic acid) - 0,60. Experiments were carried out on samples of three kinds of the Crimean limestone. Their characteristics are given in Table I.

^{*} No data on the molecular weight or viscosity of the polymer solutions are given in the paper.

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Table I. Characteristics of samples of the Cretaceous limestone from deposits in the Bakhchisaraj district, Crimea (mean values out of 10 estimations)

Kind of limestone	Density $\rho \times 10^{-3} \text{ kg/m}^3$	Exposed porosity β (%)	Water-absorption W (%)
I. Microgranular, white with a yellowish tint, texture spotty	$2,08 \pm 0,01$	$21,2 \pm 8$	$10,2 \pm 0,4$
II. Of different granulation with microgranular cement, almost white, texture irregular	$2,19 \pm 0,02$	$15,0 \pm 1,0$	$7,4 \pm 0,5$
III. Microgranular, slightly dolomitized, grey, texture massive	$2,10 \pm 0,03$	$18,4 \pm 1,4$	$8,7 \pm 0,8$

The limestone samples cut in the form of a cube with 5 cm ribs were emerged into vessels with solutions reaching up to one third of the samples' height. The vessels with the PBMA solutions were covered with a polyethylene film in such a way that about one third of the sample was outside. The solutions were changed starting with less concentrated (10%) and passing to more concentrated ones (15% and 20%) as the sample mass in the solutions of given concentration stopped increasing. 20% solution could not be obtained in the xylene and ethanol

mixture because the dissolubility of PBMA in this mixture is limited. Therefore, in this case, 10% and 15% solution were used. The impregnation with BMK-5 solutions was done in a similar way, only in the solution's vapour. Here, in a three solvents mixture were used 5%, 7,5% and 10% solutions, in mixture of four solvents - only 5% and 7,5% ones. Drying in the initial period was retarded. In test samples estimated were the changes of their mass in the process of impregnation and drying, the changes of their waterabsorption and bending strength after the treatment with the polymers. The waterabsorption was evaluated as percentage increase of the sample's mass after keeping the sample in water during 3 days at room temperature. The data on the changes of the samples mass and waterabsorption are given in Table 2.

The data indicate that the resulting saturation of the limestone with a polymer solution depends upon the exposed porosity of the sample which is shown in the Table through waterabsorption. The drying process depends upon the nature of the solvents, first of all upon their volatility. The samples impregnated with xylene and alcohol-xylene PBMA solutions become almost completely dry during 10 weeks in the conditions of retarded drying under bellglasses. It means that in passing to open air drying, the solvents evaporation rate curves showed the same even regularity (Fig. I, N°1 and N°2). White spirit in closed conditions evaporated very slowly, while in passing to open air drying showed a sharp increase in the evaporation rate (Fig. I, N°3).

The amount of the polymer which remains in the samples after treatment, apparently, depends upon both the polymer nature and its degree of polymerization and upon the nature of the solvents, that is, upon the factors determining the size and shape of the polymer's molecules in the solution and their ability to penetrate into the

Table 2. The change of the mass and waterabsorption of limestone samples after treatment with PBMA and BMK-5

Kind of limestone	Polymer	Solvents	The increase of the sample mass after impregnation (%)	The increase of the sample mass after impregnation and drying (%)	Waterabsorption W (%)		Decrease of waterabsorption after treatment (%)
					Before treatment	After treatment	
I	PBMA	xylene	10,0	3,3	10,0	7,3	26,5
		xylene-ethanol (1:1)	9,9	3,3	10,3	7,2	30,0
		white spirit xylene (9:1)	8,8	2,6	10,2	7,6	20,8
	BMK-5	3 solvents	8,8	0,56	9,8	2,5	74,5
		4 solvents	8,6	0,52	9,7	2,95	69,6
II	PBMA	xylene	8,5	3,0	6,8	2,6	61,7
		xylene-ethanol (1:1)	8,0	2,7	7,8	1,1	85,9
		white spirit-xylene (9:1)	7,4	2,1	7,9	5,8	26,6
III	PBMA	xylene	5,6	2,2	8,0	6,4	20,0
		xylene-ethanol (1:1)	8,0	2,4	9,0	6,75	25,0
		white spirit xylene (9:1)	5,4	2,0	7,4	6,5	12,2
	BMK-5	4 solvents	8,1	0,53	9,2	2,8	70,0

pores of the stone.

Xylene and alcohol-xylene PBMA solutions gave, approximately equal accumulation of the polymer in the limestones, the white spirit solutions somewhat less (Table 2). This may be accounted for by the poor dissolubility of PBMA in white spirit (this was the reason why xylene was added). In comparison with PBMA, the BMK-5 accumulation was 4-6 times less, though the concentrations of BMK-5 solutions were only twice as little. In this case, the decisive factor is the inability of longer BMK-5 molecules to penetrate into the porous structure of the limestone.

The decrease of the waterabsorption of the entire samples after treatment depended upon the degree to which the polymer closed the pores of the surface layer. It turned out that BMK-5 decreased waterabsorption to a greater extent than PBMA did.

The distribution of the polymer inside the stone was determined by comparing the initial waterabsorption of the samples with that of the plates produced by cutting the treated sample parallel to one of its sides (3-5 mm thick). Proceeding from the degree of the waterabsorption decrease in plates as against the initial waterabsorption of the sample, the degree of the polymer penetration and its distribution inside the sample can be estimated (Fig.2). In the limestone treated with BMK-5 the waterabsorption is lower than the initial one only in the outer plates, which indicates the peripheral distribution of the polymer. In samples treated with PBMA, all the plates show lower waterabsorption as compared with the initial one. It is a sign that PBMA penetrates into the depth of the limestone. The degree of waterabsorption decrease is the greatest in the outer plates, decreasing towards the centre. It means that the distribution of PBMA inside the sample is non-uniform. The character and

degree of waterabsorption alteration in plates, in passing from outward parts to the centre, depends on the nature of the solvents applied for the introduction of the polymer. When the plates are wetted with water, the distribution pattern of the polymer shows up as lighter or darker areas. After treating the plates with hydrochloric acid by W.Domaslowsky and J.Lehmann method, the dark areas which contain a negligible quantity of the polymer or none at all, turn out to be etched, thus giving a clear picture of the polymer distribution inside the stone (Fig.3). The most uniform distribution of the polymer occurs in samples treated with PBMA xylene solutions. The bending strength (Table 3) in samples treated with PBMA increased, on the average, by 40%. No strengthening was observed in samples treated with BMK-5.

Table 3. The change of the bending strength of the samples of limestone group III after treatment with PBMA and BMK-5 (mean values out of 7-12 estimations)

Treatment	The polymer content (%)	Bending strength $R \times 10^{-5}$ (N/m ²)	The strength increase of the impregnated sample (%)
Untreated sample	-	129 [±] 16	-
PBMA in xylene	2,2	196 [±] 30	154
PBMA in xylene-ethanol mixture (1:1)	2,4	179 [±] 19	138
PBMA in white spirit-xylene mixture (9:)	2,0	179 [±] 24	138
BMK-5 in ethyl acetate-acetone-xylene mixture (1:1:2)	0,5	112 [±] 18	absent

Conclusion

1. The impregnation of limestone with the solutions of polybutyl methacrylate of low viscosity grade by means of the "suction" technique with the following retarded drying results in deep penetration of the polymer and consolidates the stone. The most effective is the treatment with xylene solutions. A higher molecular copolymer BMK-5 under the same conditions consolidates only a thin surface layer of the limestone.
2. For experimental evaluation of the polymer distribution inside porous materials, the data on the waterabsorption decrease (or exposed porosity) in separate plates obtained by cutting the treated sample in comparison with the initial waterabsorption (or exposed porosity) of the sample can be used.

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Legends to the Figures

Fig. I. Drying of the limestone samples treated with PBMA solutions.

Mass of the solvents evaporated ($m_1 - m_x$) is referred to the mass of a sample after impregnation m_1

1 - xylene - ethanol mixture (1:1);

2 - xylene; 3 - white spirit - xylene (9:1).

Fig. 2. Limestone waterabsorption decrease inside the treated samples

W_0 - a sample waterabsorption before treatment;

W_a - the waterabsorption of a plate produced by cutting the treated sample.

Fig. 3. Results of hydrochloric acid etching of the limestone plates produced by cutting the treated samples

Rows: 1 - PBMA in xylene; 2 - PBMA in xylene-ethanol mixture (1:1); 3 - PBMA in white spirit xylene mixture (9:1); 4 - BMK-5 in the mixture of 3 solvents; 5 - BMK-5 in the mixture of 4 solvents.

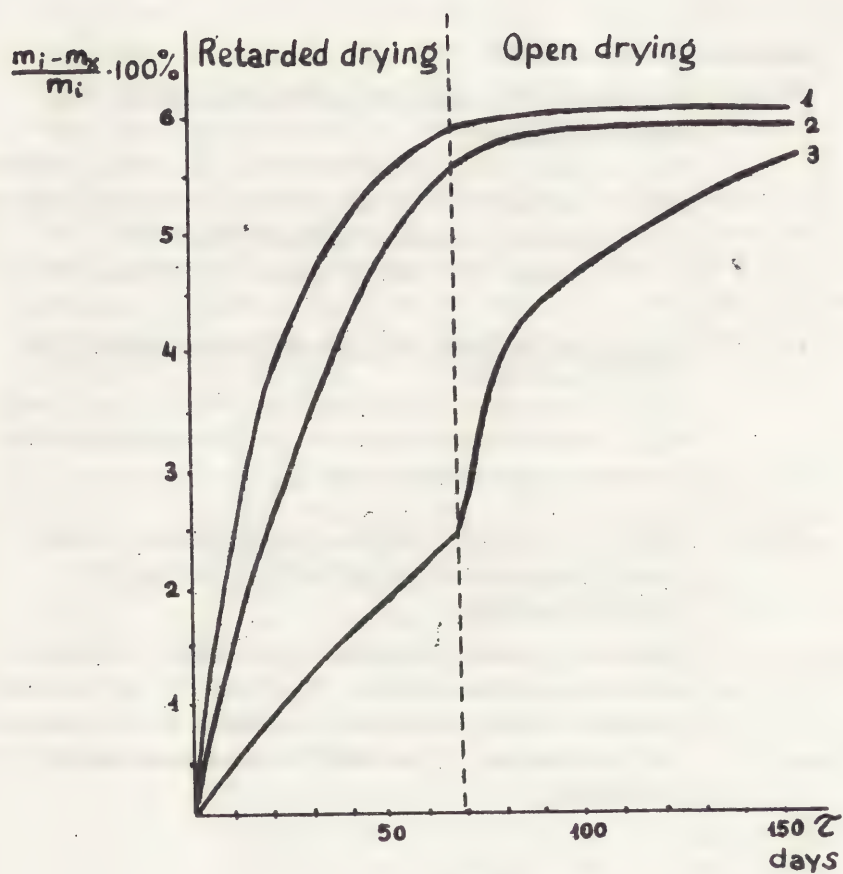
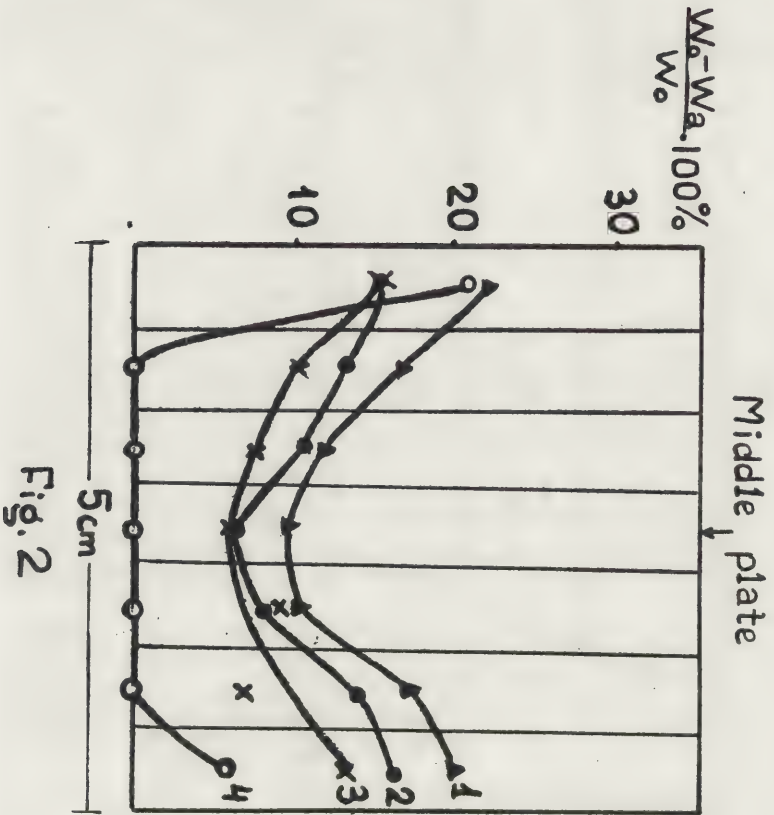


Fig. 1



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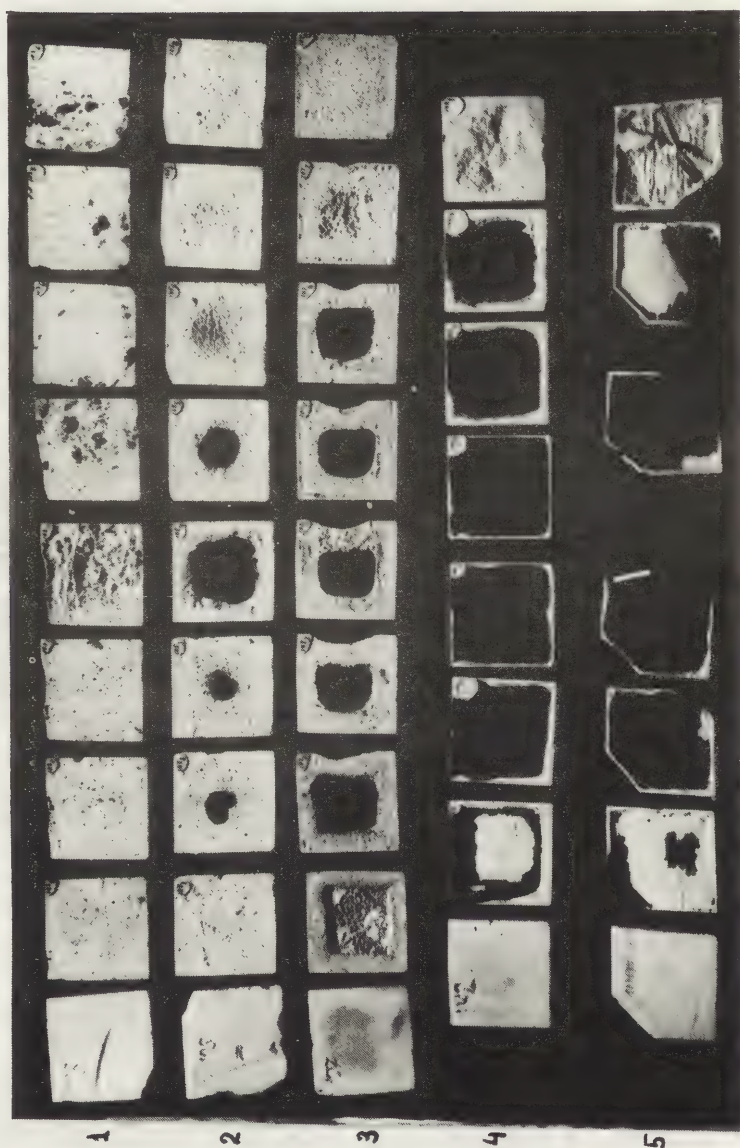


Fig. 3

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THE CLEANING OF THE FACADE OF THE
TUSCHINSKI THEATER IN AMSTERDAM
(AN APPLICATION OF ON COMPLEXING
AGENT BASED PASTES)

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Zagreb, 1978



THE CLEANING OF THE FAÇADE OF THE TUSCHINSKI THEATER
IN AMSTERDAM (AN APPLICATION OF ON COMPLEXING AGENT
BASED PASTES)

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Abstract

This article deals with the application of on Complexon 111 based pastes on a ceramic art-Déco facade.

Carefull execution of the cleaning of monuments is only possible when visual interpretation is completed with scientific data.

Aspects in cleaning of buildings

It would be a good thing when the cleaning of monuments, or parts of them, was limited to objects where the filthiness, accumulated in the course of time, can cause an accelerating disintegration in the future.

Certain aspects may influence the dicision to clean a building or not. There are, e.g., aesthetical aspects, and commercial aspects. Are not, after all, the buildings of commercial firms or, even better perhaps, the buildings of the cleansing-firm itself, thought to express the reliability and cleanness of those firms? H. Hörman (1) says, and quite rightly so, that there are also the risques of uncontrolled action when too much reserve towards cleaning is being practized. Approaching the cleaning of a building in such a way can cause severe damage, contrary to an approach based on a well-considered, carefully executed and scientifically supported cleaning.

Hörman, in his in 1956 written article, gives more of such worthy remarks.

Mr. P. v.d. Schuit, of the National Monument Office (Zeist, the Netherlands) drew the attention lately on article 14 of the Dutch Law on Monuments. It says, in words similar to those of Hörman, that, in restorations, no methods or means may be applied that directly or after some period of time, can cause damage to the building. Bringing the consequences of this article of the Dutch Law on Monuments into renewed attention makes it possible to exercise more influence on the use and choise of methods and means that are applied. From this point of view the authors of this article were invited to accompany and support in a critical way the preparation and execution of the cleaning of the façade of the Tuschinski Theater in Amsterdam.

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The cleaning of the facade of the Tuschinskytheatre.

The Tuschinski Theater was designed by H.L. de Jong in 1918 and finished around 1923, and has remained almost unchanged ever since. The building is known as one of the most remarkable examples of the Dutch Art-Déco period. Façades of that size, executed in ceramic material, are a rarity in the Netherlands.

A good description of the building and its interior is given by F.F. Fraenkel (2), who also states the origin of the ceramic elements. The cleaning of this façade was actuated by an exclusive first night of a Dutch feature film.

The mixed, predominantly green-bluish colour of the glazing had become covered with a layer of black dirt, and, consequently, had lost its original lustre.

It was assumed, in the beginning, that the black layer existed of organic dirt, so that it was thought advisable to clean the ceramic material with a 1% solution of non ionogene soap, as described by Stambolov, Van Asperen de Boer (3) and others (4-17).

This working method, however, did not offer satisfying results. And it appears from this that knowledge of the underground, which in this case is of a ceramic material, together with visual perception, not necessarily goes with a right judging.

Then the authors were asked to follow critically the further experiments of the façade cleansing-firms, and it was concluded that the knowledge of these firms of the making of money outran their professional knowledge. They ventured, for instance, instead of discussing openly the materials and methods to be chosen, to "prove" the harmlessness of their preparation by putting their bare hands in it. They obscured its composition in a smooth selling style. Their alarmingly fast resulting tests gave rise to serious concern. Only the use of hydrofluoric acid resulted in a "quick cleaning", thus making the composition of their cleanser very doubtful.

We directed our tests towards a good solution, using a.o. means and methods that are mentioned by Stambolov (3.16) and Lewin (14).

It then appeared from analyses, quite unexpectedly, that the layer of dirt existed of 98% sodium sulfate (gypsum), 2% metal oxide and a small amount of organic material.

The outcomes of these analyses and the surmises resulting from tests gave sufficient reason for the execution of tests with recently in the Netherlands introduced pastes that are based on a complexing agent. A complexing agent in an alkaline environment can form a chelate compound with - in most cases difficult soluble - salts of heavy metals, as e.g. calcium.

The various applications and their variants are described by J. Emmerling (20.21), T. Chvatal (18.19), T. Stambolov and J.R.J. van Asperen de Boer (3). The positive outcomes of the tests resulted in the placing of the cleansing-order with the firm that had the sole agency for this material, Messrs. Boogert, Amsterdam, who executed the cleaning in good concert with and to the entire satisfaction of the owner of the building and the people concerned of the National Monument Office. Messrs. Boogert had the façade covered, bit by bit, with a 1.5 cm thick layer of highly alkaline

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prepared paste: CA (Bauchemie, Garmisch Partenkirchen, W. Germany), which in its turn was covered with a polyethylene foil. After one day, the paste, together with the dirt, was taken away by means of brushes and hot water, uncovering the undamaged joints and glazing-surface.

Amsterdam, February 4, 1978.

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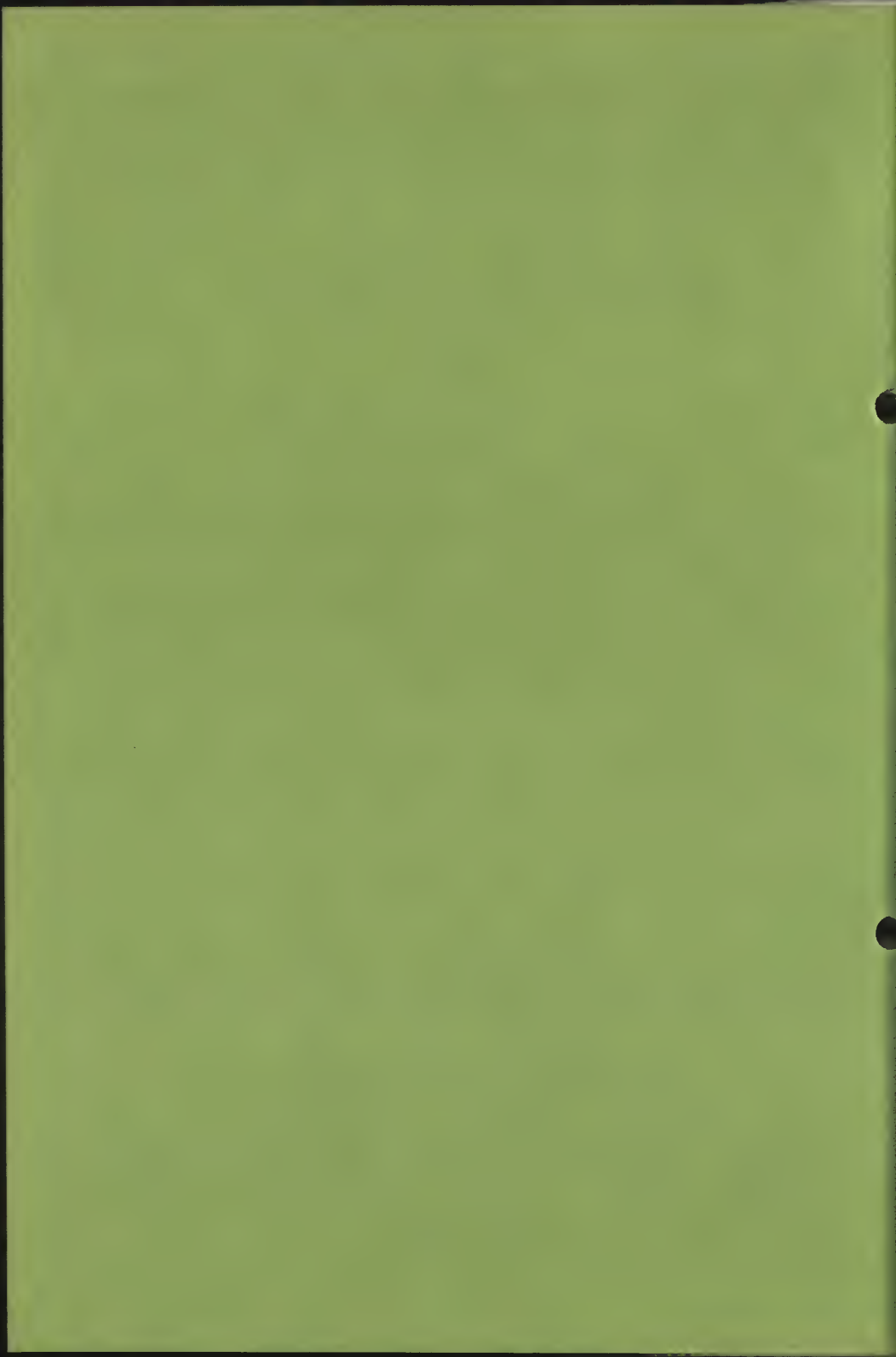
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ABOUT SOME ACTUAL PROBLEMS OF RESTORATION
OF SCULPTURE IN STONE

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Zagreb, 1978



ABOUT SOME ACTUAL PROBLEMS OF RESTORATION OF SCULPTURE
IN STONE

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The compensation of missing fragments for sculpture in stone must be based on the scientific research work, as any restoring process. Any changes or distortions in process of restoration are inadmissible, because every work of art is not only the object of aesthetic pleasure, but it is the documentary monument of history of art and culture.

The tradition of instinct compensation of missing fragments was rejected only at the boundary of XIX-XX centuries. Then the principle of scientific restoration confirmed by the documentary analogy was formulated. "There is no opposition against scientific restoration" (I. Grabar).

However, the real process of restoration remained to depend on individual creative power of a restorer. The restorer was obliged to choose the kinds of stone similar to the original because he had only traditional materials at his disposal. Besides, the sculpture had to apply to inadmissible methods in process of attaching the missing fragments: cutting out the nests, drilling the holes for iron pins and other incursion into the body of original. Thus all problems appeared at the XX century are the following: in the process of compensation

of missing fragments it is necessary 1) to choose the stone exactly of the same structure and kind as of the original; 2) to imitate the plastic forms, colours and texture of the sculpture of all times and people; 3) to repeat the individual manner of author (for example, individual impressionistic dab). All this questions needed searching for an objective, exact and safe method of compensation of missing fragments. Recently such method has been developed when synthetic materials found the use in process of restoration of sculpture in the Russian Art Restoration Centre after I.E. Grabar.

This method of restoration of sculpture in stone uses moulding and founding of missing fragments in similar synthetic material according to the identical volumetrical sculpture. This method excludes a subjective interpretation of missing fragments. The working process by the new method is the following:

1) The scientific choice of volumetrical analogy at the same or other material. The comparison of the sculpture values in the whole volume and in details. Photographing the restored work and its fragments and the analogy from various points of view. Recording all scientific, research and restoration works. Describing the state of the damaged work of art in the restoration passport.

2) Discussing and reception of previous scientific and restoration works at the restoration council. Definition of limits of compensation (it is connected with

debatable analogies which gives no rights for the restoration).

3) Moulding the parts of the analogy. Each part is corresponding to the missing fragment of the statue.

4) Founding in similar material according to the identical size.

5) Reception and confirmation of realized fragments by the restoration council.

6) Attaching of the realized fragments must be fulfilled with the same imitate material as the missing fragment.

7) The final ratification of this work by the restoration council, photographic and consecutive recording all operations in the restoration passport (with instructions for structure of the imitate material and the glue).

This method gives us the possibility

1) To exclude a subjective interpretation of missing fragments because moulding and founding exclude subjective interpretation of forms.

2) To exclude any incursion into the body of the original in the process of attaching missing fragments because of using durable adhesives and synthetic resins. The seams which appeared in the process of attaching are filled with the same imitate synthetic material.

3) To keep the integrity of visible perception; however in the process of analysis in nonvisible rays of spectrum supplemented fragments can be discovered.

The main problem appears in the process of restoration of antique sculpture. During centuries the main problem in the process of restoration of antique statues was replacing missing parts of antique sculpture and imitation antique things as much as one possibly could. However, at the boundary of XIX-XX centuries in history of art and restoration practice there was a new scientific theory about the necessity of conservation of antique statues in the same statement in which they have reached to our days. It was caused by realizing documentary and scientific value of antique sculpture, which was understood only at that time.

The decision to conserve the initial statement of sculpture inferred from the restoration practice and also from archeology and history of art (for example: analysis of restoration of Appollon Belvedere and statues from the Aegean fronton). Many museums of the world, including Hermitage, began active works to take the compensations from antique statues. It was because of distortions owing to insertions of XV-XX c. which distort the antique original hiding scientific and documentary information. This works gave good results for the history of art because many monuments were learned, systematised and reattributed. At the last time the activity with taking off the compensations became especially widespread, including the main collections of antiquities (for example, Vatican).

But there is a danger in such process: to take off

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from the original "the culture layer" which has artistic value. Taking off the compensations which were made by Michelangelo, Donatello, Verrocchio, Bernini, etc. damages our idea about their creation. It is necessary to remember that many ancient monuments which were very important for the aesthetic evolution from the XVI to the XX c. received acknowledgement only after restoration. There is no artist who didn't study at examples from classical antiquity: Laocoon, Apollon, the Medice Venus. Taking off the compensations from these statues would be a serious loss of "the culture layer".

At the same time it is impossible to recreate the initial appearance of works because of changes in the process of previous restorations and influences of external forces (spots, patina, weathering, decay). Furthermore with damage of compensations many pages from history of restoration would disappear. Besides, the conservation of compensations gives integrity to the artistic ensembles.

There is example of good conservation of the compensations which were made in the 1968-1972. It is the bust of Afrodita (1 A.D.). As a result of this restoration the scientific method of such works was elaborated. At the beginning the antique statue released of compensations was taken out of the ensemble for the scientific and historic treatment (for example, in our case three restorations were done: in antiquity, in XVIII century and at our time). Simultaneously we have made the mould of the antique

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original and attached all compensations which were of scientific or artistic value to this mould. After this the statue was returned to its place and the stylistic integrity of the ensemble was kept.

This method helps us to take off the last compensations and at the same time to keep the 'culture layer'. Later we can receive new scientific conclusions after detailed investigations (stylistic, chemical, physical, analysis in nonvisible rays of spectrum).

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APPLICATION OF POLYMER FILMS REMOVING
SURFACE CONTAMINATIONS FROM SCULPTURES
MADE OF DIFFERENT MATERIALS

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APPLICATION OF POLYMER FILMS FOR REMOVING SURFACE
CONTAMINATIONS FROM SCULPTURES MADE OF DIFFERENT MATERIALS

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The removing of surface contaminations from works of art' (made of plaster of Paris, ceramics, wax, wood, stone and other materials) very often requires much work and care on the part of the restorer, because unstable or badly preserved materials of the sculptures can be easily damaged, the texture of the initial surface changed.

According to routine work, the contaminations are washed with water solutions of detergents which must be thoroughly removed by subsequent washings with distilled water. Sometimes some organic solvents are used as cleaning agents. In all these cases, the surface of the object is rubbed with swabs or brushes. Small particles are washed away from the upper layer of an unstable material and stick fast in its pores altering the appearance and sometimes even the plastic of the object.

There is a technique of removing contaminations by applying "compresses" from absorbing materials. Some powder-like or fibrous stuffs wetted with water or some organic solvents are put on the surface of the object and left till dried /I/. The effectiveness of this method depends upon the size of the adsorbing material particles. When coarse-grained adsorbents are used, the desirable degree of cleaning is not achieved. Fine powders get stuck in the pores and cannot be fully removed from such materials as plaster of Paris, weathered marble, certain kinds of limestone and terra-cotta. Water, when penetrating into the depth of some porous material, dissolves part of

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the substances, and when it evaporates there appear some spots and salt cristallization. Local redistribution of particles may occur as well.

The surface contaminations can be removed with the help of some film-forming solutions of natural and artificial polymers. The viscous polymer solution is put on the surface to be cleaned and is left there till the solvent evaporates. The film which is formed is taken off together with the contaminations it absorbed. This method has the following advantages:

1. No mechanical treatment of the surface is necessary (rubbing with a swab or a brush);
 2. The penetration of the solvents into the pores of the material is reduced to a minimum;
 3. The adsorption effect is uniform on the whole surface.
- Of natural polymers, starch is applied in the form of a colloidal solution /2/, of artificial ones - nitrocellulose in organic solvents /3/. Starch has low microbiological stability, and, in case its particles remain in the pores of the material or in the dents of the relief, it may cause mildew growth which leaves spots difficult to remove. Besides, because of low mechanical stability, the underdried starch film is difficult to remove. When the water is fully evaporated, the film becomes hard, deformed and tears off the material particles.

The method of removing spots from marble with the help of nitrocellulose solutions does not appear to be quite satisfactory because of the solvents toxicity and inflammability of both the solvents and the nitrocellulose.

That is why, work was carried on in the State Hermitage with a view to find some polymers which are free of such shortcomings. In our opinion, the polymers to be used for receiving cleansing films must possess the following properties:

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1. Chemical inertness - the absence in the polymer of such groups which could interact with the material of the object;
2. Dissolubility in available, non-toxic solvents;
3. The ability to be combined with chemically inert plasticizers;
4. The ability to form films which during the contamination sorption would be soft enough to be easily taken off after, so as not to destroy the unstable surface of the object, and to be strong enough not to get torn when removed from the surface.

The structure and polymerization degree of the polymer must prevent its penetration into the porous materials of the object. The viscosity of the polymer solution must be such as would not let it flow down from a vertical surface.

Water-soluble polymers: carboxymethyl cellulose sodium salt (CMC) and polyvinyl alcohol (PVA) were selected for the experimental work. The choice of the polymers and their grades were determined by the above properties which are indispensable for the given aim. The solutions of the selected grades of the polymers in various concentrations were put on the model samples of plaster of Paris, terra-cotta, marble and limestone placed vertically. In the course of the tests it was found that during the drying process the film shrinks unevenly and the particles of not stable materials come off. That is why some plasticizers (glycerol or glycol) were introduced into the polymer solutions. They impart a required degree of flexibility, adhesion and stability to the film.

Using model samples, some recipes were worked out for removing contaminations from the materials of various degree of mechanical stability and preservation. The concentration of the solution depends on the polymer grade (the molecular mass) and is from 5 to 30%. To prepare

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the solution, the polymer is dissolved in water containing glycerol from 5 to 30%. If necessary, alcohol (5-15%) or ammonium hydrate (2-3%) are added. The viscous polymer solution is put on the whole sculpture surface. The water evaporation and the film-forming rates depend upon the temperature and the humidity of the surrounding atmosphere and every from two hours to two days. The film-forming solutions containing 25-30% plasticizers make it possible to remove contaminations from unstable materials. When water is completely evaporated, the film remains flexible.

The samples treated with the film-forming solutions and the films removed from them were examined under a microscope to make certain that the application of the polymer is ^{is} harmless for the material cleaned. In the cases when the recipes worked out for materials with a various degree of stability were used, no coming off of the model samples particles was observed. When the samples cleaned with film-forming solutions were compared with the control untreated ones, no changes of the material texture were detected under a microscope.

On receiving some positive results on model samples, we tested this method of removing contaminations on works having no museum value. When this method had been approved of by the Hermitage restoration council, surface contaminations from a number of the museum sculpture objects of various materials in different states of preservation were removed. Among the exhibits cleaned in this way there were plaster busts, antique and west-European terra-cotta statuettes, Ancient Egyptian limestone stelae, an antique marble sculpture with the surface weathered. The remnants of the paintings on ancient reliefs and statuettes were preliminary consolidated with thermoplastic resin solutions.

Thus, the film-forming solutions CMC and PVA allowed

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the contaminations to be removed from a number of sculpture objects with unstable surface without causing any change of the material texture. The latter would be unavoidable were washing used, rubbing with a swab or brush including. By using this method for cleaning sculpture made of stable materials, for example, marble, the quality and effectivity of work is increased by several times.

In the case when no contacts of the object with water solutions are desirable, the contaminations are removed with the films formed from alcohol-soluble polyamide (PA) grades. Some experimental work like that carried out with CMC and PVA films was done with this polymer too. The polyamide solution in alcohol (5-15%) is put on the surface from 2 to 5 times with 20-50 min. intervals. The thin transparent film being formed adsorbs the contaminations. In a thin layer, it is flexible and may be applied for removing contaminations layer after layer from unstable materials. The rate of the work with alcohol-soluble solutions is several times as great as that with water solutions. The polyamide film is especially effective for cleaning wax reliefs.

When contaminations are removed from relief and carved surfaces, a layer of the alcohol solution of polyvinyl acetate or polyvinyl acetate dispersion of plasticized grades is put on the polyamide film. A double film possesses greater stability and permits the contaminations to be simultaneously removed from a greater area of the relief surface.

Our studies in search of the effective methods for removing contaminations from works of art are being carried on.

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OF THE PROBLEM OF THE STONE MATERIAL
EROSION AND METHODS OF ITS EVALUATION

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5th Triennial Meeting
Zagreb, 1978



OF THE PROBLEM OF THE STONE MATERIAL EROSION AND METHODS OF ITS EVALUATION

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In the present work some theoretical premises for investigation of erosion of construction and other materials as a function of many variable arguments are considered. Theory of similarity and dimensions with Weierstrass theorem as well as modern methods of experimental design are used (1), (2), (3), (4), (8), (9), (10).

Investigation of erosion of various materials presents a very difficult task due to a significant number of variable arguments which describe the process under study. These arguments are acoustic wave velocity in the air (C_a), air speed (V_a), air temperature (T_a), relative air humidity (B_a), atmospheric precipitation (h), air pressure (altitude of the area) (P_a), duration of exposure to the air (t_{ac}), area latitude (φ), frequency of seismic oscillations (f), amplitude of seismic oscillations (A), duration of seismic events (t_{cs}), elastic wave speed in the sample material (C_M), duration of erosion (t_{ep}), material surface slope with respect to the horizon (α), material surface orientation azimuth with respect to the ground (α), yield stress of the sample material (σ_T), ultimate resistance of the sample material (σ_s), temperature of the sample material (T_M), relative material humidity (B_M), biological corrosion indices (β), chemical corrosion indices (X) and so on.

Thus, the degree of erosion in general form is a function of many variable arguments

$$\Delta = \Phi(C_s, V_s, T_s, B_s, h, P_s, T_{sc}, \mathcal{P}, f, A, tcq, \\ c_M, t_{sp}, \alpha, a, b_r, b_s, T_m, B_m, B, X) \quad (I)$$

Theoretical analysis of expression (I) is given in detail in references (5), (6), (7). It was stated that the use of the similarity and dimensions theory with Weierstrass theorem proves rather cumbersome and complicated when the number of variable arguments exceeds two.

For this reason, when analysing values which are functions of more than 2 variable arguments it is reasonable to use modern methods of design of extremal and interpolation experiments.

Lately, a new branch of science, the mathematical theory of experiment, was developed. One of the divisions of this branch is the design of extremal experiments. Many scientists and engineers frequently deal with extremal and interpolation tasks aimed at finding of optimal conditions for complex processes, the choice of optimal composition of multicomponent systems or mathematical description of an interpolation model of the process under study, for example, the process of erosion of construction materials and other similar complex multifactor processes.

The general form of such response function is

$$\eta = Q(x_1, x_2, \dots, x_K) \quad (2)$$

where η - is a process parameter which should be optimized or interpolated;

x_1, x_2, \dots, x_K - are independent variables which may be used in the experiment.

x_1, x_2, \dots, x_K are called factors and coordinate space with coordinates x_1, x_2, \dots, x_K is considered as the factor space (1), (2), (3), (8), (9), etc.

Reconnaissance studies showed that the most significant effect on the degree of erosion is assigned

to the following parameters of all the physical and mechanical factors (I): wind speed (V_B), air temperature (T_B), atmospheric precipitation level (h) and erosion time factor ($t_{\partial P}$).

Then (I) becomes

$$\Delta = F(V_B, T_B, h, t_{\partial P}) \quad (3)$$

or in coded units

$$\Delta = N(x_1, x_2, x_3, x_4) \quad (4)$$

where:

$$\begin{aligned} x_1 &= \frac{V_B^{BY} - V_B^{OY}}{P_1} ; & x_2 &= \frac{T_B^{BY} - T_B^{OY}}{P_2} ; \\ x_3 &= \frac{h^{BY} - h^{OY}}{P_3} ; & x_4 &= \frac{t_{\partial P}^{BY} - t_{\partial P}^{OY}}{P_4} ; \\ P_1 &= \frac{V_B^{BY} - V_B^{HY}}{2} ; & P_2 &= \frac{T_B^{BY} - T_B^{HY}}{2} ; \\ P_3 &= \frac{h^{BY} - h^{HY}}{2} ; & P_4 &= \frac{t_{\partial P}^{BY} - t_{\partial P}^{HY}}{2} ; \end{aligned} \quad (5)$$

P_1, P_2, P_3, P_4 - variation interval (step);

BY - parameter upper level;

OY - parameter basic level;

HY - parameter lower level.

On the basis of the experimental design theory and taking into consideration the four independent variable arguments one can make a plan of the full factor experiment of the type

$$N = K^q = 2^4 = 16$$

where N is number of experiments, K is number of levels and q is number of variable arguments.

The plan of the full factor experiment is presented in table I. On this basis the following regression

equation can be written:

$$\begin{aligned} \Delta = & B_0 + B_1 x_1 + B_2 x_2 + B_3 x_3 + B_4 x_4 + B_{12} x_1 x_2 + B_{13} x_1 x_3 + \\ & + B_{14} x_1 x_4 + B_{23} x_2 x_3 + B_{24} x_2 x_4 + B_{34} x_3 x_4 + B_{123} x_1 x_2 x_3 + \\ & + B_{124} x_1 x_2 x_4 + B_{134} x_1 x_3 x_4 + B_{234} x_2 x_3 x_4 + \\ & + B_{1234} x_1 x_2 x_3 x_4 \end{aligned} \quad (6)$$

where: $B_i = \frac{\sum_{u=1}^N x_{iu} \cdot u}{N}$

$i = 0, 1, 2, \dots, q,$

u - experiment number within the range of

$$B_{ij} = \frac{\sum_{u=1}^N x_{iu} \cdot x_{ju} \cdot \Delta u}{N} \quad (7)$$

$i \neq j, i, j = 0, 1, 2, \dots, q$

Coefficient B_i here shows the degree of effect of each component on response, i.e. the expected change in the response with alteration of the corresponding component from the basic to upper level (from 0 to 1 in coded units).

x_{iu} is a value equal to +1 or -1, located at the interception of column i with row u of the design matrix, q is the number of studied components (independent variable functions; in our example $q = 4$), $N = 2^q$ is the number of experiments.

All coefficients estimated using the above first order plans^{x/} are determined to the same accuracy of $\pm t \frac{S(y)}{\sqrt{N}}$ where the value of t is chosen from the t -distribution table, usually on the basis of 95% confidence probability level (5% significance level) and

x/ The order of a plan is determined according to the highest degree of the approximating polynomial which can be evaluated using the given plan.

$f = 2^q - q$ degrees of freedom.

$S\{\epsilon_i\} = \frac{S\{y^0\}}{\sqrt{N}}$ - is an error in determination of regression coefficients and $S\{y^0\}$ - are errors of experiment.

As one can see from table 1, three more basic level experiments may be added to the main full factor experiments which is of value for determination of accuracy or errors of the obtained experimental results.

For experimental investigation of regularities of erosion of art and architectural monuments, construction materials, various buildings and ground surfaces both in natural and artificial conditions we designed and built a device for measurement of the degree of erosion. The device is supplied with anchors fixed on the surface of the investigated object. A base plate with special holes for measurements of shortest distances from the base plate outer (basic) surface to the surface of the investigated object with the help of the depth gauge is firmly attached to the anchors with the nuts. A device, measuring the inclination angle of the studied surface with respect to the horizon, consisting of a stand, a dial goniometer and a plumb, is fixed on the base plate (zero surface).

Besides, the device is supplied with an aiming circle for determination of the azimuth of the investigated surface stretch.

This measuring technique allows to determine the degree of erosion in every point of the studied surface and to estimate the mean rate of erosion using the total of values for (n) points.

THE PLAN OF THE FULL FACTOR EXPERIMENT OF $2^9 = 2^4$ TYPE

Table I

Number of experiments	Design matrix																
	Responses																
	x_0	x_1	x_2	x_3	x_4	x_1^2	x_2^2	x_3^2	x_4^2	x_1^3	x_2^3	x_3^3	x_4^3	x_1^4	x_2^4	x_3^4	x_4^4
1	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
2	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
3	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-	-
5	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-	-
6	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-	-
7	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-	-
8	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-	-
9	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-
10	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-
11	+	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-
12	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-

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LES TRAVAUX ENTREPRIS SUR LES FONTS
BAPTISMAUX DE SAINT JEAN A SPLIT

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5ème Réunion triennale
Zagreb, 1978

LES TRAVAUX ENTREPRIS SUR LES FONTS BAPTISMAUX DE SAINT JEAN A SPLIT

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r é s u m é

Les fonts baptismaux ont été construits très vraisemblablement au 13^e siècle avec des dalles de remploi de sarcophages romains et 6 dalles préromanes en relief - partie de mobilier d'église probablement de la cathédrale de Split. La dalle avec la figure du roi croate témoignant de notre existence politique et culturelle précoce au sein du palais de Dioclétien, est de valeur exceptionnelle.

Les travaux se sont déroulés de 1973 à 1975 avec des interruptions. Ils furent motivés par la remise en place de la dalle avec la figure du roi, démontée pour les expositions à Paris et à Sarajevo en 1971. Mais leur but principal était de permettre un démontage simple et sans danger des dalles préromanes - soit en vue de leur sauvegarde à un moment donné, soit pour les présenter à des expositions. Cette condition préliminaire a été réalisée par une jonction des dalles à un endroit au moyen de joints en bronze, fixés par des vis et écrous dans les trous existant auparavant; les bords inférieurs des dalles ont été fixés sur un crépi à la chaux. La pierre a été nettoyée des couches de saleté, des traces de cire, de crépis et de ciment par un procédé mécanique et un lavage à l'eau distillée. A titre de mesure de

protection, en premier lieu de la dalle avec la figure du roi croate, on a réalisé une image photogrammétrique de toutes les couches, sur les six côtés, à l'échelle de 1:2. A également été effectué un moulage en résine de silicones, exécuté en pierre granulée liée avec la résine polyester KP-L, lequel servira éventuellement pour les copies ultérieures au lieu de la prise directe du moulage de l'original.

Ces travaux ont montré d'autre part que les fonts baptismaux ont été réalisés d'une seule fois et qu'au-dessous il n'y a pas de traces de baptistère antérieur.

La grande exposition " L'art en Yougoslavie de la préhistoire à nos jours " a motivé le démontage de la dalle avec la figure du roi croate sur les fonts baptismaux du baptistère à Split, en vue de présenter en 1971 au public mondial à Paris et yougoslave à Sarajevo, l'oeuvre la plus importante de la sculpture croate des premiers temps du Moyen-Age.

Grâce à cette circonstance ou plutôt à l'occasion de la remise en place de la dalle après l'exposition, il a été envisagé d'effectuer des travaux sur l'ensemble des fonts baptismaux. Les travaux se déroulaient, avec des interruptions considérables, de 1973 à 1975,

L'Institut pour la Protection des Monuments historiques de la Commune de Split, compétent pour ce territoire, a dirigé les travaux, tandis que le projet et l'exécution des travaux étaient confiés à l'Institut de Restauration de Croatie à Zagreb et à son équipe et à ses collaborateurs-experts. Les travaux de prospection et la documentation de prospection ont été exécutés par les experts du Musée Archéologique de Split, de l'Institut régional pour la Protection des Monuments historiques et de l'Institut précité de Split.

Le financement était assuré par le Fond de la République pour la Promotion des Activités culturelles,

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et par le Fond de la Promotion des Activités culturelles de la ville de Split.

Je présente les travaux effectués en qualité de conservateur d'alors et en tant que membre des Commissions pour l'Evaluation des Projets élaborés pour les Travaux de Conservation des Monuments immobiliers et mobiliers de l'Institut de la République de Croatie pour la Protection des Monuments historiques à Zagreb.

Les fonts baptismaux en pierre, construits dans le baptistère de Saint-Jean à Split - dans le palais de Dioclétien où se trouvait autrefois le temple de Jupiter - ont la forme d'une croix à branches égales avec cloison intérieure vers la branche méridionale et septentrionale, formant ainsi l'espace unique de la branche orientale et occidentale. Construits probablement au XIII^e siècle avec des matériaux de remploi, des dalles de sarcophages romains et 6 dalles de l'époque préromane, dont 4 sont ornées d'entrelacs, et 2 dalles ont, en plus des ornements de bordure, un sujet figural iconique. En effet, une dalle représente la figure du roi croate sur le trône, avec une figure debout et une figure allongée; l'autre dalle est caractérisée par un pentagramme et par les cinq doigts de la main - symboles de la Sainte-Trinité et de l'éternité. Toutes les dalles sculptées sont des parties de mobilier d'église datant de la deuxième moitié du XI^e siècle, et on suppose qu'elles sont très probablement originaires de la cathédrale de Split.

D'après un document de 1533, l'archevêque de Split, Andrija Cornelio a fermé les fonts baptismaux déjà existants avec des dalles en pierre pour empêcher que l'eau bénite ne soit salie, puisqu'alors le baptême n'était plus administré par immersion; les fonts baptismaux servaient aussi de dépôt d'eau bénite. Au cours de cette modification, les jointures entre les ,

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dalles ont été remplies de crépi rougeâtre en deux couches pour assurer l'étanchéité; ce même crépi fermait aussi la jointure sous la grande dalle qui couvrait l'espace longitudinal des fonts baptismaux en forme de croix.

Les premières recherches historiques et artistiques, ainsi que des explications et interventions de conservation entreprises sur ce monument datent de 1894.

Depuis cette époque, la figure du roi suscitait un vif intérêt et des discussions entre les savants, d'ailleurs toujours d'actualité, à savoir: s'agit-il de la figure du Christ ou du roi. Mais la plupart d'entre eux sont d'avis qu'il s'agit de la figure du roi croate, ce qui accentue particulièrement la valeur de cette dalle. Etant donné l'apparition précoce d'une telle figure dans les premiers temps du Moyen - Age sur la côte adriatique de l'Est, prouvant ainsi notre existence nationale sur ce territoire.

Notre célèbre historien d'art et conservateur, bien connu à l'étranger, Ljubo Karaman a consacré de nombreuses études et des traités scientifiques pour clarifier cette question. Grâce à la valorisation historico-artistique de la représentation du roi croate, Karaman décida, entre 1930-1931, alors qu'il était conservateur à Split, de déplacer la dalle avec la figure du côté latéral Nord de la branche orientale, sur le côté frontal des fonts baptismaux, en face de l'entrée dans le baptistère - petit temple dans le palais de Dioclétien.

En qualité de conservateur, Karaman a expliqué au public sa décision dans un article paru dans les journaux où il dit entre autres: " ainsi la dalle informera chaque étranger et chaque visiteur de l'ancien palais de Dioclétien à Split, de la vérité : que dès les premiers temps du Moyen - Age (XIe siècle), les souverains croates

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étaient des seigneurs au coeur même du palais de Dioclétien ..."¹, puis dans un autre article, exposant son attitude décisive : " ... était la pose d'un signe symbolique de la voie que nous devons suivre pour affirmer notre culture et nos droits; la faire sortir des archives poussiéreuses et de l'oubli des siècle, l'exposer en plein jour et la mettre en lumière avec tous nos souvenirs et notre peuple dans le passé! "²

En 1972, avant le commencement des travaux, les fonts baptismaux étaient tels qu'ils avaient été laissés après les travaux de conservation entrepris par Karaman.

L'idée principale de la dernière entreprise de conservation récente était centrée sur la réalisation d'un démontage très simple et correct des dalles en relief préromanes à des fins quelles qu'elles soient: en cas de cataclysme éventuel - comme condition préalable en vue des mesures de protection des dalles comptant parmi les monuments les plus précieux de notre patrimoine culturel d'une part et d'autre part pour que des dalles d'une telle importance puissent être éventuellement présentées aux expositions, sans danger pour l'ensemble des dalles et des fonts baptismaux. Tous les travaux étaient orientés vers cet objectif principal.

D'où le premier pas à faire: élaboration du plan architectonique, géodésique et de la hauteur des fonts baptismaux à l'échelle de 1:10, puis la prise photographométrique de la dalle avec la figure du souverain croate. Les photos ont été prises des 6 côtés de la dalle à l'échelle de 1:2 (caméra VWK Zeiss), isohypse avec équidistance de 2 mm, photographié à une distance de 3 m. La photo de la dalle avec toutes les couches a été effectuée par "Geoprojekt" de Split.

Après avoir démonté les dalles des fonts baptismaux, il a été procédé au nettoyage des traces de cire, de ciment, de crépi et des couches de saleté, par procédé

mécanique, à l'aide de scalpels, puis par un léger lavage à l'eau distillée.

En même temps, c'est à-dire en 1974, a été pris le moulage de la dalle avec la figure du roi croate, et ce sur les 6 côtés, par un négatif en résine de silicones (production de Wacker - Munich); le moulage a été effectué en pierre granulée liée avec la résine artificielle polyester KP-L (production de l'usine "Chromos" Zagreb). Le moulage de la dalle dans cette résine artificielle a été exécuté comme mesure de protection en vue d'empêcher la prise nocive ultérieure de copies de l'original, de sorte que les copies ont été faites à partir du nouveau moulage.

Etant donné que les dalles verticales des fonts baptismaux étaient démontées, il était possible et même indispensable de procéder à la prospection de la dalle du socle et de l'espace au-dessous et autour de la dalle. Les sondages ont montré que la dalle en marbre du fond repose sur un socle en maçonnerie élevé, tandis que le socle est posé directement sur la voûte en tuf de la crypte du temple et des traces de fonts baptismaux plus anciens n'ont pas été constatées à cet endroit.

Il a été également constaté que les fonts baptismaux sont construits d'une seule fois, ce que confirment les crampons en fer des jointures des cloisons inférieures vers la branche transversale des fonts baptismaux en forme de croix.

Dans l'espace longitudinal, on distingue clairement sur les parois des traces d'eau bénite, qui a été plus ou moins longtemps en usage, et cela est visible à des niveaux différents. Les traces les plus foncées apparaissent à la hauteur des cloisons transversales, c'est-à-dire au niveau où les fonts baptismaux étaient le plus longtemps remplis d'eau, et à cette hauteur, du côté occidental intérieur est gravée une croix à branches égales, ce qui pouvait peut-être indiquer la

nauteur admise de l'eau dans les fonts baptismaux. Les traces d'écoulement de l'eau sur les cloisons latérales indiquent que l'eau était transvasée de l'espace central dans les espaces latéraux qui ont encore aujourd'hui une vidange visible, contrairement à l'espace central.

Le but de cette conservation de démonter le plus simplement les dalles sculptées, a été résolu par l'introduction de joints en bronze fixés par des vis et des écrous dans les trous existant déjà et remplis auparavant de résine artificielle Araldit AW 106. Les bords inférieurs des dalles en pierre près du socle ont été posés et fixés sur un crépi de chaux.

L'Institut pour la Protection des Monuments historiques de Split, qui dirigeait ces travaux, était d'avis que la dalle avec la figure du roi croate du côté latéral devait être remise à sa place originale, sans tenir compte de l'endroit où la dalle se trouvait au moment de son démontage pour être exposée à Paris en 1971, ni de la valorisation à la suite des travaux de conservation de Karaman, ni de sa présentation de la dalle il y a plus de 4 décennies.

Les opinions des experts étant divergentes, au début de 1975 l'Institut de la République de Croatie pour la Protection des Monuments historiques a organisé avec ses commissions pour l'évaluation des projets élaborés en vue des travaux de conservation des monuments mobiliers et immobiliers, une consultation et une vaste discussion d'où il résulte que d'après la Loi sur la protection des monuments historiques, l'Institut pour la Protection des Monuments historiques à Split est compétent pour la solution de ce problème et la prise de décision définitive. En même temps ont été soulignées l'importance de ce problème et la grande responsabilité incombant à cet Institut.

En entrant aujourd'hui dans le baptistère à Split, nous sommes accueillis par la figure du roi croate marquant la création artistique du Moyen-Age et témoignant de l'existence de notre peuple depuis fort longtemps sur l'Adriatique Orientale.

Il reste encore à niveler le dallage de l'antique édifice du temple romain et de bien mettre en lumière le dialogue réciproque entre l'architecture romaine, les fonts baptismaux médiévaux et la statue de Saint-Jean-Baptiste par notre contemporain Meštrović dans l'ensemble des fonctions rituelles et monumentales du baptistère, qui subsistent.

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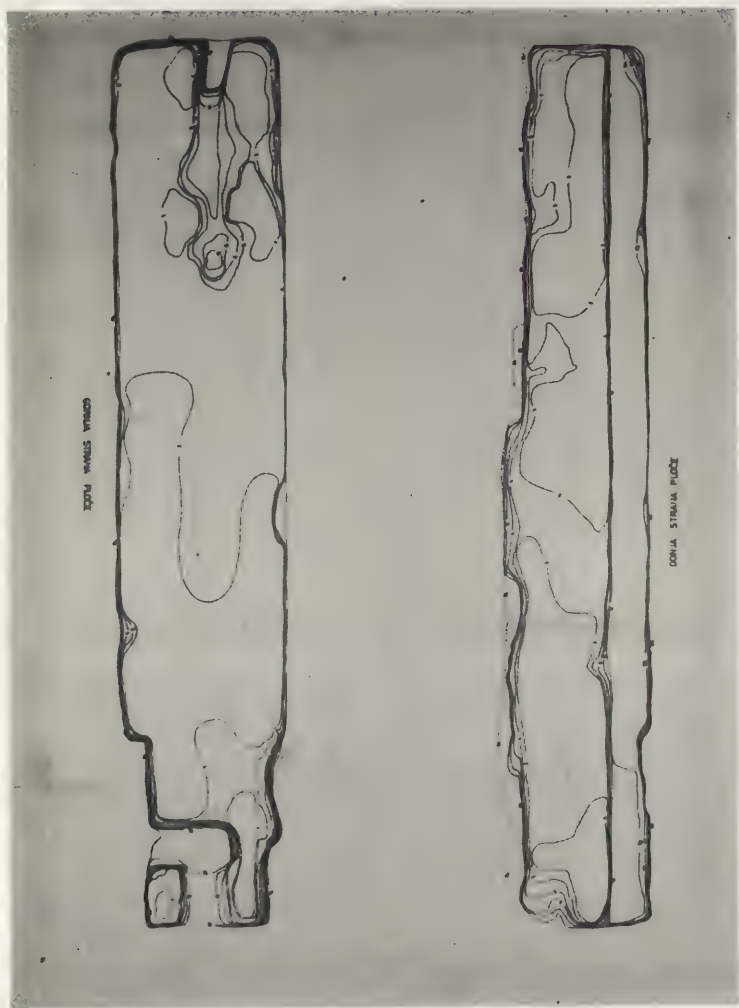


Les fonts baptismaux de Split avant les travaux. Photo:
Karlo Stühler, Split.



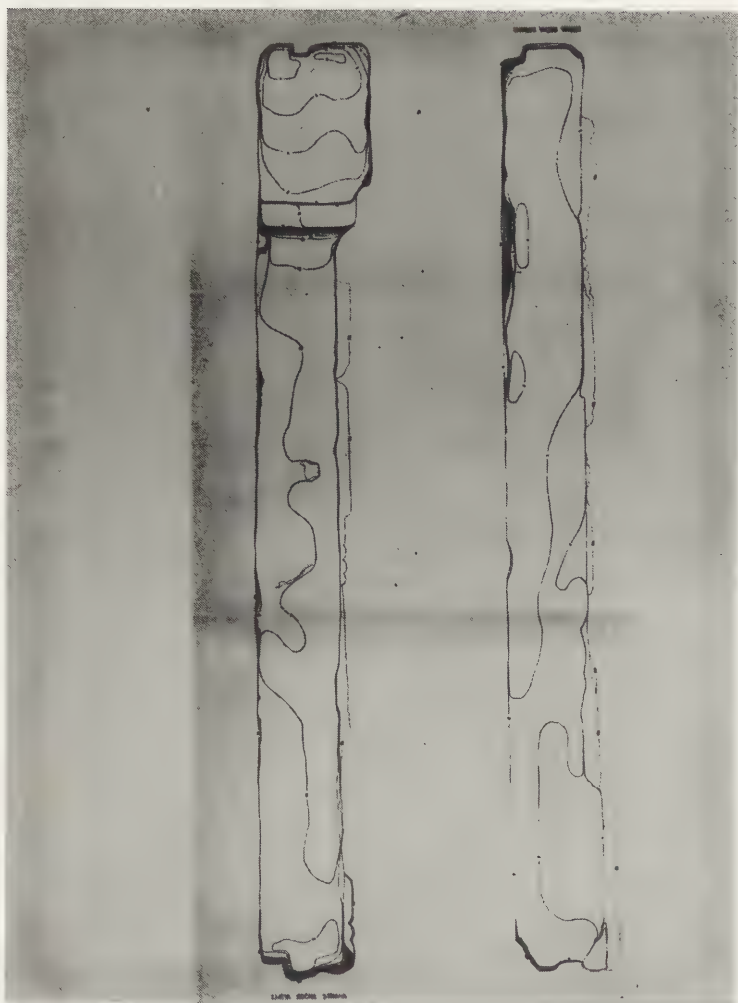
La dalle avec la figure du roi croate; la prise photo-
grammétrique à l'échelle de 1:2 effectuée par "Geoprojekt"
de Split, 1974.

78/10/10/11



Les deux côtés - inférieur et supérieur - de la même dalle; la prise photogrammétrique à l'échelle de 1:2 effectuée par "Geoprojekt" de Split, 1974.

78/10/10/12



Les côtés laterals - droit et gauche - de la même dalle;
la prise photogrammétrique à l'échelle de 1:2 effectuée
par "Geoprojekt" de Split, 1974.

78/10/10/13



Les fonts baptismaux après les travaux. Photo: Živko Bačić, 1978.



78/10/11

THE DETERIORATION AND CONSERVATION OF
POROUS BUILDING MATERIALS IN MONUMENTS.
A LITERATURE REVIEW. SUPPLEMENT 1978.

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MATERIALS IN MONUMENTS. A LITERATURE REVIEW.
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T. Stambolov and J.R.J. van Asperen de Boer

1. Introduction

The present survey of the most important literature published since early 1975 again follows the structure of the 1967/69 reports to this Committee. It is again selective and aims at drawing attention to the most important recent developments.

The English version of that review was published by the International Centre for Conservation in 1972; a second enlarged edition published in 1976 includes the 1975 Supplement (38). A Dutch translation with illustrations has been published in 1978 (39).

The increasing interest in the problem of stone deterioration and treatment has resulted in a number of international conferences. The size of the published proceedings has also grown considerably. A second La Rochelle symposium was held in 1975 with rather modest proceedings: 18 papers (2). Those of the Bologna 1975 symposium (32) contain 53 papers to 16 in the 1972 Bologna proceedings. The Athens 1976 symposium produced some 40 papers (3). Results from the June 1978 Paris conference could not be included in this review but only seem to confirm this trend: 74 papers (8). Romanovsky has criticized this rather prolific output of papers and has suggested that there should be a single international conference on stone conservation every 4 years, supported by restricted meetings on particular subjects (31). The concentration of papers in conference proceedings is probably indeed the reason why only a few articles of interest could be found in the more usual periodicals.

The multidisciplinary approach to finding the best solutions in formulating conservation programmes for monuments seems to flourish best in internationally supported projects such as for the Athens Akropolis (3, pp. 257 ff.). However, some progress can be observed on national levels as well (1). On the other hand better conservation is not automatically ensured by a larger number of researchers and a greater production of papers. It is therefore perhaps rather significant that Schaffer's authoritative 'The Weathering of Natural Building Stones' of 1932 was reprinted in 1972 with minimal changes only (35).

As in previous supplements the decimal numbering of the subheadings refers to the one used in the earlier reviews (38).

2.2. Crust formation

The role of the soluble salts as participants in the development of crusts and the disruption of the surface of stone and related materials caused by these salts, are the subject of many detailed studies. The majority of the accounts are preoccupied with the behaviour of the hydrated salts, mainly the sulphates, and also with their origination which, it seems now commonly accepted, stems from either the ground water enriched with sulphates, or air pollutants of mineral content. Among the latter, sulphur dioxide gas receives most attention (12, 13, 18, 37). The debate in which these authors are involved concerns the mechanism of rupture formation in crusts as well as in the underlying stone or in other mineral porous materials. Some investigators assert that the damage is done by the pressure of hydration inherent in the salts capable to crystallize with the retention of a number of water molecules, and seem to have designed their tests according to their need of results that would support this view (5 - see the statement of S.Z. Lewin in the discussion appendix of this paper). Others (5) argue that, on the contrary, it is the total volume of salts deposited at the stone surface that is responsible for the decay of stone. Measurements, cited by these authors, supply evidence that a given volume of sodium chloride deposited in the surface of a stone, produces equal damage to that caused by that same volume of sodium sulphate hydrate ($\text{NaSO}_4 \cdot 10 \text{H}_2\text{O}$) or gypsum ($\text{CaSO}_4 \cdot 2 \text{H}_2\text{O}$). Hence the explanation that the cause of damage is not to be sought in the hydration-dehydration phenomenon but in the process of crystallization and recrystallization of the salts and the resulting mass transport and migration of material into the stone. The point of view of Lewin (5) appears to be in agreement with the findings of Pauly (30) in connection with the corrosive effect of the chlorides; salts that, in contrast to the sulphates, do not hydrate. On account of his experimental basis Pauly (30) assumes that sodium chloride (NaCl) favours the dissolution of already deposited salts, as sodium sulphate hydrate and gypsum, through a not yet clarified interstitial activity performed during the crystallization-recrystallization stage. This is illustrated by the observation that a gypsum crust cracks and peels off more rapidly according as the content in it of sodium chloride increases.

Important in this respect is also the additional observation that a gypsum deposition tends, by an increasing content of sodium chloride in it, to slightly redissolve. Furthermore, sodium chloride disturbs the transition temperature that governs the system gypsum-anhydrate. If then sodium carbonate is present, it reacts with solid gypsum and this leads to the formation of deposits of calcium carbonate and sodium sulphate. Thus according to Pauly (30) the crystal metamorphosis (gypsum-calcareous stone-gypsum) that takes place via the interaction between sodium chloride, sodium carbonate and sodium sulphate should be recognized as the decisive factor that accounts for the deterioration of the type of stone i.e., limestone which was the subject of his study.

3.2.2. Transport of liquid water

Pauly (28, 29, 30) made extensive studies of the influence of rain on the deterioration of monuments and applied theoretical considerations to actual churches in La Rochelle and Paris.

3.6. Determination of moisture

Measurements of the microclimate surrounding monuments or statues have been reported in some cases. Fondelli et al. (14) described a project to investigate the deterioration of statues in the Boboli gardens in Florence by measuring e.g. the distribution of wind and rain, surface and air humidity, the chemical composition of the rain and by photogrammetrically controlling the surfaces of the statues.

Alessandrini et al. (4) took into account the climatic conditions in Milano from the early 19th century on in studying the decay of marble used in the Milan cathedral; data on the microclimate around the cathedral were lacking, however.

Boekwijt (6) studied the effect of heating on the moisture content of plasters in seven monumental Dutch protestant churches. Continuous heating at room temperature was found to cause considerable drying out of the plaster. It is recommended to heat only a few degrees continuously in winter and to warm the building as quickly as possible for the divine services.

4.3. Wind erosion

Pauly (28, 29, 30) has studied weathering phenomena characterized by localized pulverization (maladie alvéolaire). A correlation was attempted between the composition of the attacked stone and local rain impact and wind turbulence in a number of monuments in France.

4.5. Deterioration by biological agents

During the 1975 Bologna symposium 9 papers presented related to biodeterioration among these a study of damaging processes of the Karnak temples in Egypt (11).

4.6. Quality of building stone

Mamillan has reported the application of a number of physical measuring methods to evaluate the deterioration of stone in monuments proposed earlier by him (23). He discussed especially applications of measuring the propagation of sound in situ to assess the mechanical cohesion of the stone.

5.2.6. Chemical cleaning

In a clear article provided with an appendix on stone cleaning recipes, Lewin and Rock (20) elucidate the rules that control the cleaning of stone with chemicals. And although they are primarily concerned with the removal of iron stains, the authors also offer various other important conclusions that are of significance for the cleaning of calcareous stone in general. For instance, to be effective phosphate containing cleaners of iron stains must be acidic. Yet because of this very acidity they will attack and etch calcareous stones, while, in fact, they are the stones (limestone, marble) that are most often discolored by iron. Oxalate containing cleaners will, upon prolonged contact, likewise convert the surface of a calcareous stone to calcium oxalate monohydrate; this will tend to separate from the underlying stone. Fluoride containing cleaners also cause damage owing to their acidic reactivity required for such use. At the zones of contact they transform the calcareous stone in a crust of calcium fluoride which is porous and has a tendency to spall. This side-effect may, however, be avoided through regulation of the time of contact (9). The fluoride cleaner is, to that end, applied not as a liquid, but as a paste, i.e., a mixture of hydrofluoric acid and a suitable filler. In order to improve the performance of this cleaner as a remover of objectionable crusts on calcareous stones (usually a porous layer consisting of dirt and gypsum bound together by efflorescent calcium carbonate) some formic acid is also added because of its property to dissolve calcium carbonate quickly (40). A formulation for optimal cleaning of crusts on calcareous stone should, therefore, be in agreement with the above stated guide-lines. Chvatal (9) proposes a paste that is prepared by mixing 5-10% of hydrofluoric acid with 5-10% formic acid and a filler (resistant to fluoride).

Chvatal (9), moreover, elaborates on the cleaning properties of the sodium salt of ethylenediaminetetraacetic acid as removers of crusts containing predominantly gypsum. In this context he puts to use his discovery that, that same chelating chemical dissolves about four times as much gypsum as it does calcium carbonate, and then proceeds to compose an alkaline (pH 12.6) paste which contains:

- 30% aqueous solution of the sodium salt of ethylenediaminetetraacetic acid
- a filler with a large internal surface, for instance attapulgite
- a film-builder such as a polyvinylacetate dispersion
- a surfactant.

According to the degree of pollution Chvatal (9) recommends to apply from 3 to 6 kg per square meter of cleaning paste on the stone surface and to cover it with a plastic foil in order to retard a premature drying of the paste. The paste may be left for several weeks on the stone so that it could penetrate the crust - this being of no danger whatsoever to the stone. The foil bands with the paste adhering to them are then peeled off and, if desired, a conservation treatment follows. A certain broadening of the employment of this paste, is attained by the addition of some fungicide as it enables the paste simultaneously to remove algae and lichens. Hoke (19) likewise reports successful tests with the chelate cleaners.

Besides gypsum crusts the chelating agents will remove very rapidly and effectively iron stains, provided they are correctly employed in accordance with their chemistry. The knowledge, for example, that a chelating agent, already having sequestered bivalent iron/ Fe^{++} / would quickly and easily dissolve a deposit of tri-valent iron/ Fe^{+++} /, and that an iron stain is just that, is used of to compose a liquid that will remove very obstinate iron stains from porcelain in less than 2 minutes. The stain remover is formulated as follows (16):

- 7.00 g $\text{Na}_2\text{H}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ -sodium orthophosphate (needed to produce a pH of between 1.5 and 4.5, required as operating condition)
- 71.60 g H_2O
- 24.30 g Na_5DTPA -sodium salt of diethylene triaminepentaacetic acid (chelating agent)
- 2.80 g H_2SO_4 conc. (contributes, as sodium orthophosphate does, to fix the pH value in the range 1.5-4.5)
- 36.00 g methanol - optional - (solvent of grease and similar substances)
- 0.75 g sodium salt of dodecylated dibenzene disulphonate - optional -(detergent)

0.75 g o-phenylphenol - optional - (disinfectant)

A remover of iron stains, as a powder, is also formulated:

30.00 g NaHSO_4 -sodium bisulphate

18.82 g NaHCO_3 -sodium bicarbonate (needed to produce effervescent gas that would dislocate the iron containing stain)

15.00 g $\text{Na}_2\text{H}_2\text{EDTA}$ -sodium salt of ethylenediaminetetraacetic acid (chelating agent)

10.98 g $\text{NaHSO}_4 \cdot \text{H}_2\text{O}$ — $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ -mixed salt of sodium bisulphate and ferrous sulphate

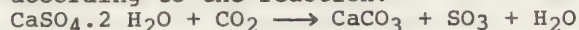
2.40 g o-phenylphenol

0.19 g sodium salt of dodecylated oxibenzene disulphonate.

The powder is added to 3 l of water in which then the object (porcelain) to be cleaned, is immersed.

5.3. Consolidation and protection

A new approach to treat the surface of calcareous stones covered with gypsum incrustations is proposed by Skoulikidis et al. (36). They have devised a treatment which implies the conversion of gypsum to calcium carbonate according to the reaction:



In connection with this procedure, the following is of interest:

- the reaction takes place (in an autoclave - hence only statues, ornaments, etc. have so far been handled in this way) at 25°C and a carbon dioxide gas pressure of 1 atm.
- the reaction is rapid and easy to carry out if in the gypsum a small amount (about 0.1%) of calcium carbonate is present. It serves as nuclei around which the calcite crystals are formed and then proceed to grow.
- there is evidence that the calcite crystals formed thus follow epitaxially the crystals of the marble on which the gypsum crust has previously been accumulated.
- by means of this technique the surface of marble statues attacked by gypsum can be regenerated without any loss of contour.
- using this method, pieces of marble attached to each other by means of gypsum paste containing 5% by weight of calcium carbonate, may be bounded together. Also fissures, crevices and the like, may thus be filled up and restored.
- gypsum copies may be superficially converted to calcium carbonate and, in this way, rendered more resistant to outdoor exposure.

5.3.4. Silicone esters

Although no specifically new products seem to have been developed in the period under review, various publications digress on this theme, presumably with the intention to

advise the users how and in which cases silicone esters should be used with the expectation of good results. Lists of available silicone esters have been published, critical characteristics of many of them, modes of application and many other aspects have been extensively discussed in the literature (7, 10, 19, 21, 22, 41, 42).

5.3.7. Synthetic polymers

Tests and achievements reported comprise already known products. Silicone resins (24, 25, 33, 34), acrylics (25), silicate-acrylic copolymer (33), epoxy resins (15, 33) have all been thoroughly investigated with regard to their applicability as consolidants for weathered stone. Their performance as such is also assessed.

An improved method of impregnation decayed stone sculpture with silicone resins was elaborately described by Hempel (17), while the consolidation of sandstone tombs, likewise with silicone resin, was reported by Nonfarmale (26). These experiments might be instructive for restorers faced with similar problems.

Finally, the ingenuity of Oddy et al. (27) in impregnating limestone sculptures with polyethylene glycol in order to render them insensitive to the effects of humidity in indoor display rooms as well as to facilitate repetitive routine cleaning of their surface deserves to be mentioned.

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HISTORY AND THEORY OF RESTORATION

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QUELQUES PROBLEMES METHODOLOGIQUES DE
LA RESTAURATION DE LA PEINTURE MURALE
ET DE LA SCULPTURE EN BOIS ET EN PIERRE
AU MILIEU DES MONUMENTS HISTORIQUES

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Zagreb, 1978

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PIERRE AU MILIEU DES MONUMENTS HISTORIQUES

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En Hongrie la protection des monuments historiques est déterminée par voie de décret-loi et d'autres règles de droit édités depuis la deuxième guerre mondiale, qui déclarent que les monuments historiques sont les souvenirs caractéristiques et irremplaçables du passé historique de notre patrie, et sont à protéger ensemble avec les oeuvres de beaux-art et d'art décoratif s'y rattachants, mettant l'accent sur l'importance égale des points de vue d'architecture, d'histoire, d'archéologie, des beaux-arts, d'art décoratif et d'ethnographie.

Comme ces règles de droit constituent la base de notre travail de protection des monuments historiques et définissent son territoire d'activité, ce n'est pas un effet du hasard, qu'après la guerre - en parallèle avec les restaurations architecturales, par malheur partiellement forcées - la restauration du matériel des beaux-arts a aussi commencée presque en même temps. Mais nous devons mentionner, que cette activité n'est pas arrivée à la hauteur ni en volume, ni en niveau - du moins au commencement - de la quantité et le niveau des restaurations d'architecture. Le développement de son organisation était aussi plus lente, mais enfin nous sommes arrivés, que l'organisation hongroise de la protection des monuments historiques, l'Intendance Nationale des Monuments Historiques est devenue de nos jours - je peux peut-être dire sans immodestie - une des bases la plus importante de l'activité de restauration dans notre pays. Pendant le cours des années prirent naissance nos propres ateliers de restaurateur de sculpteur des pierres, et plus tard de peintures. A côté de nos propres ateliers l'Intendance Nationale des Monuments Historiques donne de l'emploi à des restaurateurs, qui ne sont pas employés en permanence, affectant des grandes sommes par années à ce propos.

En parallèle avec les tâches de plus en plus nombreuses et de plus grande volume la restauration de beaux-arts en Hongrie s'est développée suivant les tâtons du commencement - après son enfance - lentement à ce degré, que les spécialistes ne s'occupent plus seulement du travail pratique: de même les restaurateurs, que les historiens d'art.

En 1965 dans l'organisation du Comité En Principe de l'Histoire d'Architecture de l'Académie des Sciences de Hongrie eut lieu une séance de deux jours, intitulée "La Carta de Venise et la protection hongroise des monuments historiques". Bien que sur cette conférence on a discuté

premièrement les problèmes et les principes et méthodes d'architecture et d'urbanisme, quelques interventions ont trouvée place, qui essayait d'analyser la méthodique des restaurations de beaux-arts d'après point de vue de principe.

Et depuis aussi on trouve des initiatives, spécialement depuis l'établissement du Centre des Restaurateurs de Musée et Méthodique. On discute pendant les conférences des restaurateurs et dans le cadre des stages : d'été, organisées annuellement, avec la participation de spécialistes internationaux, les plus importantes questions en principe de la restauration et des concernantes études reçoivent places dans les publications. Mais tout cela ne veut pas dire, que nous avons examiné le problème en toute sa profondeur, regardant tous ses aspects. Nos problèmes concrets surgissants en connexion avec les travaux certifient, que dans les problèmes en principe et méthodique ils naissent en grande diversité de conceptions, et plusieurs fois même opposées.

Je pense ici premièrement à ça que dans la formation des règles et des méthodes de la restauration des matériaux de beaux-arts appartenants au bâtiments des monuments historiques et formant avec ceux une unité - peinture murale, sculpture de pierre, installations de bois: des autels, des chaires - nous devons être guidé par deux considérations fondamentales.

Regardant les rapports étroits entre l'architecture et les beaux-arts sur ce terrain, la restauration doit prendre modèle sur les principes de tous temps des restaurations des monuments historiques, au moins partiellement. Et ce fait peut être sur un point déjà un point de vue déterminant.

Le bâtiment et en général le rôle fonctionnaire de l'architecture est d'une haute importance. Les restaurations des monuments historiques - les restaurations d'architecture - ont une importante exigence, leurs condition est de retenir la fonction correspondante, ou en cas de nécessité l'assurance d'une nouvelle.

Le bâtiment doit ainsi servir pour les exigences d'une fonction définie, et en parallèle la restauration de beaux-arts doit aussi réaliser ces exigences. La nécessité des compléments, la choix de leur technologie est très souvent en rapport direct avec la fonction /par exemple la plastique architecturale/ et ça annonce généralement une complètement de plus grande mesure. Mais le problème que jusqu'où nous pouvons aller, où se trouve la limite, par delà la valeur usuelle du bâtiment ne peut plus jouer un rôle définitif, est un problème plus difficile et à décider individuellement.

L'autre considération - d'après mon avis - laquelle doit être toujours prise en observation chez le comment de la restauration: font les régularités intérieures des différents genres de beaux-arts, qui - prenant la définition de Goethe - "donnent une occlusion de structure à l'oeuvre d'art" et lesquelles aucun artiste ne peut laisser inobservées, s'il ne veut pas lui même détruire son oeuvre.

Si le restaurateur veut tenir en considération l'ordre intérieure de l'oeuvre qu'il va reconstruire et aussi la forme extérieure correspondante, or c'est une condition indispensable de la bonne restauration, alors sa possibilité unique est l'adaptation maximale, la capacité d'intuition. Il doit trouver cette mesure de l'intervention, qui augmente encore authentiquement l'effet de la présentation de l'oeuvre et ne change rien dans son contenu, dans la quintessence de ce qu'il a à dire, dans son ordre de composition et dans sa forme de son apparition. Puisque si il arrive un changement dans aucun des énumérés, l'oeuvre restauré peut radicalement différé de l'originale créatrice: peut devenir faux, mensongé ou tout à fait autre chose.

La présentation des monuments historiques suggère beaucoup de problèmes en outre des mentionnés ci-dessus. Ces sont: le rôle du public récepteur de l'oeuvre restauré, ses exigences, ses besoins, qui en effet peuvent aussi influencer - si seulement indirectement - la sélection des méthodes employées.

Un problème important est - spécialement regardant les relations hongroises - la présentation de plusieurs périodes l'une à côté de l'autre, et ainsi la formation d'un nouvel état, d'un nouvel ordre esthétique.

Je vais donner des informations de tous ceux, a cause des cadres déterminés, chez l'examen des genres, des branches d'arts spéciaux.

Ci-apres je vais examiner la peinture murale, c'est-à-dire la restauration des peintures murales des points de vue mentionnées ci-dessus. Je voudrais partir de ça, que la peinture murale a essentiellement une destination double.

Premièrement elle s'incorpore comme branche d'art décoratif et figure dans le développement spécial de la peinture et joue un rôle important dans la formation des valeurs technique, formelle et de contenu. Elle fait témoignage des programmes décoratifs et figuratifs de l'époque en question, et de cette attitude fondamentale, qui définit la relation des époques spécifiques avec la réalité. En conséquence la peinture murale est très souvent pas seulement un document d'art, mais aussi un document direct d'histoire, qui fait revivre la vie des

tout les jours avec une force d'expérience entraînante, des plus petits détails au plus grandes perspectives.

La peinture murale est en même temps aussi un art appliqué, qui dans le cadre d'architecture exprime son commentaire, s'y ajustant et le formant. Ces contraintes indiscutables renferment des possibilités immenses. Elles donnent pas seulement à l'architecture des valeurs esthétiques sans pareille, mais à la peinture murale aussi, puisqu'il s'ouvre une circonstance presque illimitée regardant les mesures et l'effet du développement de l'art réellement monumental.

Il se montre clairement de tout les deux destinations, que dans l'objet d'art les côtés esthétiques et historiques sont réellement inséparables, c'est-à-dire la valeur esthétique est elle même aussi une catégorie historique. Mais je ne veux pas discuter ici ce problème plus profondément. Mais les choses relatées ci-dessus certifient cette dualisme aussi, que l'oeuvre de beaux-arts se démontrant ensemble avec les monuments historiques, avec des bâtiments historiques, en ce cas la peinture murale, est soumise en dernière instance à une régularité duale, résultante une fois des relations extérieures, et la deuxième fois d'intérieures.

Elle doit suivre l'ordre intérieure de son propre genre et doit en même temps s'accomoder organiquement, harmoniquement, allant de soi dans l'espace architectural, augmenter avec sa propre valeur esthétique et artistique l'effet esthétique de ce dernier.

Regardons un exemple le plus typique et ainsi le plus naturel l'espace architectural baroque et son accessoire typique: la peinture murale.

Le caractéristique de composition intérieure de l'architecture baroque est - au contraire du caractéristique classique, en générale à la fois d'un ludice spatialité -, que les différents éléments architecturaux composent une chaîne, se suivants dans le temps. L'espace ne se montre pas en une seconde, le système spatial pose à tout instant un obstacle au procès de la contemplation, mais seulement à ce degré, que l'espace puisse se dégager en mouvement, dans la série plus résolutive des images picturales dans son plein effet artistique. "L'interférence des détails de l'espace, des vues analogues à des présentiments avec la promesse des expériences encore cachées séduisent l'imagination à la solution de l'ordre spatiale, pour gagner finalement l'expérience de la plénitude, l'expérience de la perfection de l'expression" - écrivait un de nos architectes remarquables, qui est hélas mort depuis cela. Tout ça donne une possibilité naturellement pour l'exploitation complète de la réalisation de grand clavier des effets pictural, et des possibilités picturals et permet l'-

utilisation des éléments d'illusion.

Et ici, sur ce point s'attache la peinture dans la composition d'espace de l'architecture. La peinture murale, qui enfonce dans ce cas l'espace concrètement limitée par les éléments architecturaux et donne l'illusion de l'aggrandissant d'un espace complémentaire. Elle reprend très souvent le rôle typique de l'architecture et réalise au lieu d'un vraiment existant espace architectural un espace illusionniste, alors concrètement continue et fini la formation d'espace commencée par l'architecture. C'est ainsi que l'architecture et la peinture réalisent ensemble un espace composé - partiellement réel, partiellement d'apparence - et ces deux font comme conclusion finale ensemble "l'oeuvre d'art".

En conscience de tout cela examinons maintenant les problèmes de restauration du genre, sur les peintures murales baroques, qui se trouvent en Hongrie aussi dans grands nombres /et ça veut dire chez nous pour la plupart le 18ième siècle/.

Les principes initiaux de la protection des monuments historiques se trouvent établies dans la Carta de Venise. La Carta est clairement rédigée et a formulé quelques principes initiaux, ainsi ça aussi quoi nous comprenons sous la conservation, et quoi sous la restauration. Je voudrais maintenant m'occuper avec la dernière, comme nos problèmes examinés se présentent sur ce territoire.

Ils appartiennent dans le champ notionnel de la restauration tout ces interventions, qui changent l'état existant en quelque mesure. Ils entrent dans cette catégorie commencé des réinforcements structurales avec des procès modernes jusqu'à la mise au jour et présentation des époques précédentes, des compléments, ainsi que l'addition des parties nouvelles à l'oeuvre originale.

De ces opérations énumérées examinons maintenant le complètement. Nous appelons complètement ce procédé quand nous remplaçons une partie élémentaire manquante du monument historique dans l'intérêt soit d'unité structurale, soit formelle, soit pour faciliter l'intelligence des parties fragmentaires. Le complètement, en sens stricte, présume dans la pluralité des cas des parties existantes originales, au contraire desquelles les compléments ainsi en quantité, qu'en effet sont poussés à l'arrière-plan.

Il faut faire référence à ce que j'ai dit déjà auparavant, qu'en Hongrie à cause de notre histoire agitée nos monuments historiques, spécialement nos peintures murales étaient dans leur plupart mise au jour dans un état fragmenté de sous des crépissures de plus tard, ou ont souffert de grandes détériorations. Cette der-

niere ce concerne sur nos peintures murales du 18ième siècle.

Si nous prenons la notion de la restauration dans le sens le plus stricte, alors nous devons garder les objets d'art avec complètement de petite mesure, qui ne touchent pas l'essence de la peinture, c'est-à-dire dans leur forme restante. Mais généralement en Hongrie l'opinion s'est formée, que exactement regardant les peintures murales de l'époque analysée, ces peintures perdent leur essences laisser dans leurs états fragmentaires, c'est-à-dire quelle puissent poser la couronne comme la continuation organique de l'espace architectural sur cet espace intérieur, le finissant et le refermant complètement. Ainsi alors - d'après mon opinion - si les parties existantes renferment tout ces indications, qui définissent le tout univoquement, alors la mesure de la complètement n'est pas à prendre toujours en relation de quantité, matérielle, mais regardant l'importance, la prédominance des parties existantes.

Des ci-dessus ils résulte tout de suite un problème nouveau. De quelle façon doit-on faire le complètement? En générale nous prenons pour le principe initiale le plus important, que la partie à remplacer doit être univoquement à distinguer de l'original. La solution technique, la forme de cette distinction est accepté généralement: pointillement, pointage, etc. Mais la réalisation de ces éléments extérieures formelles doivent être faite d'une façon, que les additions ne diminuent pas les valeurs esthétiques de l'oeuvre d'art, ou - horrible dictu - ne forment pas un oeuvre d'art parfaitement nouveau, et avec cela une nouvelle valeur esthétique historique, qui est déjà une tâche très difficile.

Le problème de la mesure et du comment de la complètement s'annonce aussi chez la restauration de nos peintures murales de moyen âge. Pourtant nous pouvons parler ici d'une relation toute autre de l'architecture et de la peinture regardant leurs formes, on pourra même rido d'une forme contraire.

Notre matériel de peinture décore généralement des intérieurs d'églises. Les types des églises de cette époque sont - dérivant de leur fonction - généralement longitudinales. La forme centrique est devenue plus importante que dans certain époques, chez des bâtiment d'église longitudinale, suivant sa fonction, est le choeur, tout se dirigent vers ici. La formation de l'espace d'intérieure - en cas de plusieurs nefs aussi - est claire et lucide, et forme un ordre stricte et rationnel. La closure des murs, les cadres architectoniques ne sont pas percer la décoration picturale. De plus le plus importantes caractéristiques sont les suivants: l'abstention des effets augmentés de perspective, ou exactement le

manque absolu de la perspective, des compositions de touches créées avec relativement peu de motifs, le rythme tranquille, les groupements représentés avec des traits accentués, ou au plus dans un plan, éventuellement dans un espace simple, fortifient cette délimitation et font ressortir les éléments architecturaux. Et ce que concerne les figurations, je crois que je ne dois pas spécialement souligner, que le programme iconographique des images fortifie seulement la conception d'architecture: l'accentuation du choeur, en plaçant ici toujours la plus importante partie du programme figuré, dans la direction duquel se dirigent et montrent tout les autres images.

Dans les travaux de restauration de nos peintures murales du 12-13-14^{ème} siècle, qui sont retrouvées la plupart fragmentées, ou au moins très endommagées, notre problème n'est pas alors l'unité des deux arts associés - de l'architecture et de la peinture -, nous reconstruisons à cause de l'intransigeance de l'apparition de l'espace, ou en autres mots: nous complétons des plus grandes parties manquantes, naturellement à la base de documents authentiques.

La tâche à remplir est de montrer les peintures se dégageant en fragments de tel façon, qu'elles ne donnent pas un effet de touches sans raison, colorées, mais qu'elles rendent aussi dans leur fragments le rôle original de couvrir les murs, et au lieu des panneaux troublants, ou le flou des peintures, elles déploient au moins dans notre imagination la représentation originale. La façon de la représentation doit être de la sorte, que l'oeuvre d'art, dans ce cas la peinture murale - mais la même exigence est valable pour les oeuvres de la sculpture aussi - soit délectable pour tout le monde, et ne donne pas seulement une expérience documentaire-historique, mais aussi esthétique-historique.

Je voudrais mettre l'accent sur ce qui est le plus important, la conservation complète possible de la substance actuelle et de l'état original du monument. Ça assure le crédit, la valeur artistique et historique de l'oeuvre d'art. Ce principe reconnu partout dans le monde, reçoit encore plus grand accent entre les relations hongroises, en conséquence de la destruction, c'est-à-dire l'endommagement de grande mesure de nos monuments de peinture murale. Ainsi l'exigence de conservation des parties originales en étant original est chez nous encore plus que d'autre part une nécessité impérieuse. Il suit de la position d'esprit ci-dessus, que les panneaux murales originaux conservés reçoivent peu de complètement nouvelle... Nous pouvons fixer strictement que les panneaux originaux sont à conserver dans leurs état patiné, alors on doit éviter rigoureusement toute sorte de repeinte, ou surpeinte.

Jusqu'ici tout ça est univoque et claire, et une exigence réalisable dans la pratique aussi. En conclusion c'est ce qu'on peut appeler au fait la conservation.

En plus la conservation, prit rigoureusement, dans la restauration exige dans 90 pourcent des cas aussi d'autres interventions: le remplissage des trous plus petits manquants et des plus grands disturbants, ainsi que leur retouche, si en manière distinguante aussi. /Les plus petits ou plus grands touches de remplissage claire résultent en que la peinture devient généralement décomposée, vide de sens et indéléctable./

Similairement on peut, et suivant au juste les points de vue mentionnées ci-dessus de la présentation, il faut aussi compléter ces détails, qu'on peut exactement définir.

Les questions restent maintenant que:

1./ jusqu'ou peut aller le restaurateur sur le territoire de complètement?

2./ où est la limite, en passant laquelle il naquit une nouvelle valeur esthétique-historique, différent de l'oeuvre original?

Je pense pouvoir déclarer à la base de nos expériences, qu'on peut aller dans tout les cas jusqu'à ce point, où la représentation fragmentaire devient appropriée à une raisonnable - rédignons ainsi - "reconstruction theoretique", laquelle se forme dans la conscience du spectateur automatiquement pendant la contemplation.

Comme résultat définitive nous arrivons alors dans tout les cas au problème le plus important, au point cardinal de la restauration - pour nous - : que peut ajouter la restauration, c'est-à-dire notre époque, à l'oeuvre original, et pas au dernier rang, de quelle façon. Le succès ou l'insuccès de la restauration est lié à cela. Parce que le complètement doit se faire de sorte qu'il s'accorde parfaitement dans sa conception, dans son esprit à les idées de son créateur du temps jadis, qu'il peut rester subordonné, ne doit pas créer, mais - je n'y trouve pas une meilleure expression - "réproduisse", approchant avec humilité adéquate l'oeuvre original. Et c'est valable pas seulement sur les oeuvres de la peinture, mais de la sculpture aussi. Je pense qu'à côté de cette exigence, soit elle aussi rigoureuse, mais quand-même une exigence de deuxième ordre, que les complètements examiner de près doivent être univoquement et facilement à distinguer.

Si nous repassons dans l'esprit tout ça encore une fois ce que je viens de dire en examinant quelque problèmes de la restauration des peintures murales, et j'ai essayé de signaler certain base de principe et leurs con-

séquences, j'éprouve le sentiment, que je ^{ne} pourrais ^{pas} difficilement donner une réponse univoque à les questions posées. Je pense qu'il faut prendre une résolution dans tout les cas concrets en conscience des principes ci-dessus et avec leurs méditation nouvelle, ainsi qu'avec la connaissance approfondie de l'oeuvre d'art, correspondante à la situation donnée. En résultat définitive le bon succès de la restauration dépend toujours du restaurateur, de son capacité d'intuition et d'adaptation, de sa sobriété et de son sens artistique.

Pendant la restauration de nos monuments historiques les investigations nouvelles des couches des 19ième et 20ième siècles souvent résultent en des plus vieilles, plus valeureuses couches. Souvent pas seulement une, mais plusieurs, l'une sur l'autre de différents époques.

La Carta de Venise déjà citée - naturellement regardant premièrement les restaurations d'architecture - déclare, que nous devons partir de la position d'esprit, qui défini que sur le monument historique on doit respecter les compléments de tout les époques. En meme temps nous ne pouvons pas tenir tout les couches historiques également valeureuse, en conséquence également à conserver. Durant l'estimation, à la formation de la solution finale il faut apprécier deux sortes de points de vue. L'une est: la présentation d'une période antérieure, où de la faire valider appropriément demande des sacrifices - et des quelles - au détriment des époques suivantes. Dans cet égard la Carta prescrit la plus grande vigilance et déclare expressivement, que de pareilles sacrifices ne sont pas permettantes que dans des cas exceptionnels, alors quand les parties à éloigner ont une valeur minime, jusque la période la mise au jour signifie des documents de grande valeur historique ou artistique.

L'autre point de vue a apprécier est que quel est l'effet de la présentation éventuelle des différentes périodes l'une à côté de l'autre en même temps sur l'apparition uniforme du monument.

Regardons cela peut-être sur un exemple concret, que comment se pose cette question à la territoire de beaux-arts. Je pourrais citer beaucoup d'exemples intéressants et caractéristiques de Hongrie du domaine de la peinture murale, mais maintenant examinons un autre genre de cette point de vue, la restauration de la sculpture sur bois.

Pendant la reconstruction de l'église du moyen-âge d'un petit village hongrois /Mátraszőlős/ notre attention était attirée sur l'installation de trois autels et une chaire. Il est devenu sûr après d'examinations

de dimension restreinte, que sous les transformations du 18^{ième} siècle et sous la peinture à l'huile grise et laide on trouve des autels du 17^{ième} siècle, rester presque intacts.

De point de vue historique il n'était pas douteux, que pour nous l'état du 17^{ième} siècle est le plus valeureux. Nous avons très peu de monuments historiques de cette époque, la situation historique ne favorisait pas les arts et ces peu d'oeuvres, qui se formaient dans ce siècle, étaient anéantis, ou les époques suivantes les ont transformés.

Faisant disparaître les surédifications de petite mesure du 18^{ième} siècle et enlevant le repeint sans caractère l'un des autels a servi avec une surprise inattendue. Nous avons trouvé sous l'extérieure vilaine, grise, fade: des panneaux peints, aux couleurs éblouissantes, riches en fleurs: des tulipes, des grenades, des différents motifs de décorations de feuilles et de rinceaux se changent sur l'autel. Ce sont tous des éléments décoratifs de la nommée "renaissance fleuri" hongroise, c'est-à-dire dans ce cas concret ses rejetons tardifs. Cette peinture riche ne tire pas ses origines de la même époque, nous pouvions observer deux couches différentes, l'une sur l'autre, du 17^{ième} siècle.

Alors le problème était donné. De dessous la robe caractéristique - à la fin - nous avons reçu une surface montrant un état encore jamais vue. La question était maintenant que quelle chemin devions nous choisir? Devons nous ôter, détruire la deuxième couche du 17^{ième} siècle pour présenter un état homogène, dérivant du même époque? Ou laissons l'état mise au jour?

En étudiant et discutant plusieurs fois le problème nous avons décidé d'accepter la deuxième solution. Nos arguments étaient de conséquence du fait historique, notamment que nos monuments historiques et artistiques ont été détruits, que tout les fragments que nous trouvons de ces siècles remplissent avec contenu des taches blanches et à la base de ces fragments se mette ensemble lentement une unité uniforme, qui est l'histoire des arts de cette époque, se composant des pierres de mosaïque. La présentation des deux couches juxtaposées, représentant une valeur égale, illustre les changements dans le temps du monument historique.

Le peu de temps qui me reste m'empêche de mentionner tous nos problèmes. Mon but n'était pas de donner une solution aux problèmes ramifiants en principe et méthodique de la restauration des beaux-arts. Ma point de vue initiative était de mettre sur le tapis des problèmes, affronter ces difficultés, prise en considération la situation et les données spéciales hongroises, ainsi que certains principes fondamentales, en générale et historiquement.

78/11/2

THE HISTORY OF THE RESTORATION OF
PAINTINGS IN POLAND 1919 - 1939

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5th Triennial Meeting
Zagreb, 1978



THE HISTORY OF THE RESTORATION OF PAINTINGS IN POLAND
1919 - 1939

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The paper deals with the restoration of the paintings in Poland in the period when this country became again independent after almost 150 years of being partitioned by three powers: Austria, Prussia and Russia. The situation of the country as well as of the national monuments and relics was very difficult. The reasons of that were many years' negligences and enormous war devastations /1914-1918/ namely four million people killed, serious damages in the industry, agriculture and monuments of architecture. The losses of relics were caused not only by their devastations, but also many of them were taken abroad by the enemies. That difficult situation was also caused by the lack of uniform administration and legislation, very random cataloguing of national monuments etc. The serious problem was also the small number of people able to restore works of art, their poor professional knowledge and lack of state restoration workshops. In addition to this the society had little concern for national monuments. As is customary in Poland the principle of saving what had already been saved was followed.

The first after the world war ten years had a motto: "to save from devastation" i.e. to protect everything what had been saved. In the next ten years period, which coincided with the economic recession in the whole contemporary world, there occurred a strong reduction of funds allocated to culture and thus to the protection of national monuments. This could be seen, among other things, in the reduction of employees and of financing for the restoration of monuments etc. The bigger share of the burden for the restoration of monuments then fell upon the shoulders of the private sector of society which to a large extent financed the renovation of works of art.

The general principles followed in the restoration of paintings were those lively discussed in the XIXth century and at the beginning of the XXth century, and which still prevailed, namely the principles of "renovation" and "conservation". By "renovation" was meant restoring the painting to its original appearance; by "conservation" was meant preservation of the existing state and the protection against further deterioration. The official publication of the Ministry of Art and Culture entitled: "Protection and conservation of monu-

ments" /Warszawa, 1920/ endorsed the ideas and methods popularized by Aloiz Riegel, Jerzy Hager or Karol Buś. Some changes and new ideas, however, were in evidence. In general, it could be said that between 1918 and 1939 the following principles were compulsory:

- /1/ The problem of restoration of monuments is, for the greater part, a strictly artistic one; therefore it must be the work not only of a knowledgeable man but also of a skilled artist.
- /2/ In the restoration of movable works of art only minor renovations are permissible, and the alteration of its form and colour are forbidden.
- /3/ Only tested methods should be used without any experimentation. Good restoration does not depend upon the knowledge of new methods.
- /4/ The state of the work of art prior to its restoration should be documented.
- /5/ Restorations can be decided upon only by competent authorities.
- /6/ The greatest danger to any work of art is its performance by incompetent hands; accordingly it was decided not to employ the services of amateurs or novices.

In spite of these avowed principles still the education continued to be a type of self-study and "apprenticeship" under the direction of masters. This system of professionalization allowed for individual improvisations and pseudoscientific "secrets".

Some efforts to start the schooling of restorers of painting were done since 1935 by assistant professor /later professor/ Jan Hopliński at the Laboratory of Technology and Painting Techniques of the Academy of Fine Arts in Kraków. He was able to some extent to build upon the proposals for the establishment of national schools of restoration which had been put forth by W. Martin /*Alt-Holländische Bilder*, Berlin 1921, pp.156-157/ and A. Wolters /*Die Ausbildung von Restauratoren für die Museen, "Kunstchronik und Kunstmark"*, 1926, pp.46-47, 697-699/, as well as upon the programme carried out by R. Mancina: "Schema di programma per opere d'arte" /R. Mancina, *Essame delle opere d'arte ed il loro restauro*, vol.1, Milano 1936, pp.244-247/.

In the period from 1918 until 1939 there were in Poland only few restoration workshops employing on an average 1-4 persons. In Kraków the National Museum and the Wawel Royal Castle had such workshops, in Warszawa - the National Museum and the Royal Castle, in Poznań and Lwów - the local museums as well.

Polish professional magazines from that time /1919-1939/ although they were published over a rather short period contributed to some extent to the restoration of national monuments. In 1924-1925 there appeared in

Lwów some issues of "Conservation News" published and financed by a conservator B. Janusz. That magazine was edited with great care but because of financial difficulties crashed after a short time. Between the years 1926 and 1929 there was published under the same title "Conservation News" a supplement to the magazine entitled "Earth", an organ of the Polish Tourist Society. The main merits of this supplement consisted in collecting and popularizing materials and descriptions of particular monuments, mainly of architecture, and their conservation. There were many scientific expectations connected with publishing since 1930 a magazine "Protection of Works of Art" edited by the Ministry of Religions and Public Education" under the editorship of the General Conservator J. Remer. The introduction read: "The proper restoration of national monuments will not be successful unless the citizens are inculcated with a love and reverence for the relics of the past. Our magazine is intended to be a bridge of understanding between society and the restorers". The magazine was edited for only two years /1930-1931/, so the problems of restoration thereafter could be discussed only in periodicals dealing with other disciplines or in popular-scientific ones. Because of that the articles about the work and output of Polish restoration in 1918-1939 appeared rarely and were scattered among various periodicals.

The more important positions concerning the restoration of painting from that period were: by J. Chyczewski "Remarks on painting and conservation of church ornaments" in "Museum of Chełm Diocese" /Muzeum Diecezji Chełmskiej/ 1938, 6-7; by S. Dettloff "Why do church monuments vanish?" in "News for the Clergy" /Wiadomości dla Duchowieństwa/, 20, 1933, 3; by J. Hopliński "Regeneration of sepulchral picture of Wierzbicka from Ruszcza" in "Museum Diary" /Pamiętnik Muzealny/ 1936, and "Restauration d'une peinture sur bois au Musée National de Cracovie" in "Museum" 37-8, 1938; by J.P. "On the application of photography and roentgenography for examining pictures" in "Industry and Craft" 2, 1922, 1; by Z. Kacprowski "From the world of techniques and inventions. Technical and scientific bases of expertise and protection of works of art" in "Weekly Illustrated" /Tygodnik Ilustrowany/ 1929, 40; by T. Kruszyński "Renovation and coronation of the miraculous picture in Mieronice" in "Time" /Czas/ 1937, 138; by B. Marconi "Application of X-rays for the examination and conservation of pictures" in "Polish X-Ray Review" /Polski Przegląd Radiologiczny/ 1937; and "The application of X-rays for conservation of the picture of the Madonna with the Christ-Child and the founder bishop Lubrański" in "Bulletin of History of Art and Culture" /Biuletyn Historii Sztuki i Kultury/ 1935, 1; and "Removal of the surface repaints

under the control of ultra-violet rays" in "The Yearly Museum" /Rocznik Muzealny/ Warszawa, 1938; by P. Markiewicz "On the conservation of the miraculous picture of Our Lady of Częstochowa" in "The Podole Diocese News" /Wiadomości Diecezji Podolskiej/ 1926, 4-5; by N. Pajzderski "Improper conservation of the pictures painted on wood and canvas" in "Museum Diary" /Pamiętnik Muzealny/, Kraków, 1938, 7; by J. Przeworska "On the conservation of works of art" in "Earth" /Ziemia/ 1930, and "Wood fungi, their danger to works of art, and methods of their removal" in "Conservation News" /Wiadomości Konserwatorskie/, a supplement to "Earth", 1929, 9; by J. Remer "Conservation of the picture of Our Lady of Ostra Brama", Wilno 1927; by T. Rutkowski "Basic remarks on conservation of painting" in "Protection of Works of Art" /Ochrona Zabytków Sztuki/ 1930, 31, part 2; by J. Starzyński "On the wall-painting restoration in a church in Łowicz, formerly belonging to the Jesuits" in "Protection of Works of Art", 1930-31, part 1; by J. Świencicki "Methods of conservation of distemper paintings in the National Ukrainian Museum in Lvov" in "Museum Diary" /Pamiętnik Muzealny/, Kraków 1934; by W. Terlecki "Restoration of paintings by Hans Suess from Kulmbach /at St. Mary's Church in Cracow/" in "Światowid" 1932, 36; by W.S. Turczyński and T. Rutkowski "Restoration of the miraculous painting of Our Lady of Częstochowa", Częstochowa 1927, etc. In the late thirties the Polish Museum Association put forward a proposal to publish a collective work entitled "Museology" which would deal, among other problems, with conservation of museum collections. This book appeared only after the war, in 1947 and it included the works by T. Reyman on restoration and conservation of pre-historical monuments, by R. Mękicky - on weapon restoration, by J. Hopliński - on painting restoration, etc.

As early as at the end of the XIXth century conservators used to meet at various conferences, exchanging opinions and experiences. In the years 1919-1939 only such one meeting took place - that was the Restorers' Assembly in 1927, which attracted participants from all Poland. The assembly discussed mainly the problem of a social and state protection of monuments. Only little attention was paid to restoration itself, although three papers on the subject of interest were presented there: by T. Rutkowski "Restoration of pictures", E. Tor "Courses for craftsmen on the need and methods of conservation and restoration of movable works of art", and by W. Zarzycki "Picture restoration from the technical point of view".

This period 1918-1939 did not abound in scientific and technical achievements, which was due to lack of specialists and funds. In 1923-1924 there were the first attempts to X-ray paintings - B. Marconi, for example, practised it in a Warsaw hospital. Before the outbreak

of the war in 1939, radiological investigations were far advanced. A surface-rotary X-ray method was initiated in the National Museum in Warsaw in 1938. Thanks to this new method a shadow of a reverse side of a picture /e.g. flooring blocks or painting at the back/ could be removed from a radiogram. In 1938 B. Marconi worked out the first project of a device adapted to a Centix apparatus /a medical device Centalix-Phillips-Portable 56kV, 4.5 mA/ and F. Walkowski's firm in Warsaw built a frame which would make a screen and a machine movable.

The following specialists informed about ultra-violet rays applied in the examination of works of art - Kacprowski /"The world of technique and invention", in "Weekly Illustrated" 1929, 40/, W. Biernacki /"Photography as a help to jurisprudence" in "Polish Photographer" 1930, 1/ and B. Marconi /"Removal of surface repainting controlled by ultra-violet rays" in "Annual of the National Museum in Warsaw" 1938, 1/.

A. Neuman in his article "Ultra-violet photography applied to archeology" /Polish Photographer" 1938, 8/ informed about ultra-violet rays applied in the examination of works of art, among others - from the Tyszkiewicz's collection. Dactyloscopic investigations were already known in Poland in those days. J. Skoczkowski in his paper "A margin of forgery" /"Polish Photographer" 1933/ predicted that fingerprint files would help to fight forgers, and he even put forward certain proposals how such a system could be set up.

Let us see now what means of restoration were used to impregnate a wooden ground, apart from a formerly used sublimate solution in spirit or a mixture of thymol, spirit and alum. It was very common to keep a ground in a heated alum solution /up to 90°C/ for 12-14 hours. After exact rinsing it was dried, then impregnated with linseed oil with some drops of turpentine and finally coated with a mat varnish. A ground was very often reinforced with wax applied after it had been dried. During the restoration of the epitaph of Wierzbicka from Branice in 1936 sodium silicate /sodium water glass/ was used for impregnation. The ground was impregnated with warm sodium silicate every ten days for about two months. Obviously, the ground became strongly alkalized under the influence of sodium water glass impregnation.

Tumefactions in a canvas ground were removed by moistening and ironing the reverse side of a picture with a warm iron. 0.5% solution of warm glutenous glue introduced by means of a sprayer was also used.

Canvas paintings were supplemented mainly on a wax mass, or on a starchy adhesive.

To supplement mordent losses, two kinds of fillers were used: /a/ oil filler consisting of 1 part of linseed oil, 1 part of Chinese white, 2 parts of chalk and 1 part of alabaster gypsum. /b/ glue-water filler consisting of 3 parts of 10% solution of glutaneous glue in water, 10 parts of chalk and 1 part of alabaster gypsum with the addition of linseed oil.

Paintings were cleaned by turpentine and lavender oils, oil of cloves, benzine, ammonia, turpentine oil together with copaiba balm or by mixture consisting of 1 part of turpentine, 1 part of spirit and 0.5 a part of copaiba balm. In order to remove repaintings from a picture it was coated with copaiba balm and then placed in a regeneration box for quite a long time.

After pictures had been cleaned they were varnished with a mat varnish and then pointed. This varnish constituted an insulating coat which was to enable future restorers to wash off pointing immediately, if necessary.

Very often a coat of varnish was removed: /a/ employing a dry method i.e. mechanically, and /b/ employing a wet method i.e. using a solution consisting of 1 part of copaiba balm and 1 part of ammonia, or 2 parts of spirit and 1 part of turpentine, or 1 part of wine spirit and 2 parts of turpentine oil.

Resin-oil varnishes were regenerated by sunlight or by the light of a quartz lamp. Pettenkofer's method of varnish regeneration was becoming less and less popular.

The period 1919-1939 was of great importance for the documentation of restoration. Such a problem arose, for example, in Rome in 1930 at a conference on scientific methods of examining and restoring works of art. Not only was the importance of documentation in restoration emphasized there but it was also stated that no picture would ever be protected without having been photographed beforehand. Coming back to the situation in Poland it should be mentioned that restoration documentation was very well carried out in the Restoration Laboratory of the National Museum in Warsaw. It embodied a description of the state of a work of art, results of scientific and technical studies, a course of restoration, it had an index according to authors, schools, number in a catalogue and the owner. The documentation was supplemented by numerous photographs. The best and most thorough restoration documentations were published - for example, an article by B. Marconi entitled "Microchemical and spectral investigations of dyes applied in the 16th century picture - the Holy Family with a Lamb - a copy from a Raphael's picture" /Annual of the National Museum in Warsaw, 1938/. Another article of this type was completed by J. Hopliński - "Regeneration of a sepulchral picture of Wierzbicka from Ruszcza conducted in a restoration laboratory in the National

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Museum in Kraków" /Kraków 1937/. The years 1919-1939 brought a deep conviction of the need for preparing a thorough photographic documentation and formal records on the course of the restoration, specifying all the materials used during the process.

At that time Poland was in the process of rebuilding from the very foundation every phase of life. It can be affirmed that despite such serious difficulties the restoration of painting compared favourably with that of many other European countries. The generosity of society and the devotion of the majority of the restorers /among others B. Marconi, J. Hopliński, M. Słonecki, T. Rutkowski, E. Trojanowski/ managed to compensate for the limited funds granted by the government.

It must be kept in mind that in depicting the situation of restoration in Poland in the years 1919-1939 not all the interesting problems could be here included because of a summary nature of the present paper.

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PROTECTION AND RESTORATION OF CULTURAL
AND ARTISTIC MONUMENTS OF CENTRAL ASIA
IN THE FIRST YEARS OF SOVIET POWER
(1917-1924)

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5th Triennial Meeting
Zagreb, 1978

PROTECTION AND RESTORATION OF CULTURAL AND ARTISTIC MONUMENTS OF CENTRAL ASIA IN THE FIRST YEARS OF SOVIET POWER (1917-1924)

B.Ya. Stavisky

During the fifty years that elapsed since the annexation of Central Asia by Russia before the Great October Socialist Revolution an extensive effort was undertaken in searching for and studying of cultural and artistic monuments of Turkestan, the name for Central Asia in those times. A lot of work was carried out by prominent Russian researchers, Prof. N.I.Veselovsky, Prof. V.A.Zhukovsky and, especially, Academician V.V.Bartoltz, who laid the foundation for scientific studies of Central-Asian history in general. Local lore enthusiasts of the region, V.L.Vyatkin, B.N.Kastalsky, N.P.Ostroumov, I.T.Poslavsky and other members of TALC (Turkistan Archaeology - lovers Circle) found in 1895 also made a sizable contribution.

Their activities were, however, carried out under the conditions of lacking state legislature on protection of Central-Asian cultural monuments and far too rarely enjoyed the support of the authorities. Much depended on personal inclinations of this or that chief of the Tsarist colonial administration.

If, for instance, Governor-general A.B.Vrevsky (1889-1898) patronized the TALC, another high official, A.V.Samsonov (1909-1914), declared, after sightseeing in Samarkand, for everyone to hear: "The sooner all this is ruined the better it will be for the Russian State system".

After the establishment of Soviet power in Central Asia the new people's administration usually re-

lied in cultural matters on the same scientists and local lore experts who used to work in the region before the Revolution. But the attitude towards cultural and artistic monuments changed abruptly for their examination and conservation were immediately recognised as matters of governmental importance. Under the influence of Lenin's Decrees local legislative Acts concerning Central-Asian cultural and artistic monuments were formulated in 1918-1924. Modelled on Central Russian authorities engaged in governmental protection of cultural heritage similar Central-Asian governing bodies were established.

Decree 116 of the Council of People's Commissars (CPC) of the Turkistan Republic, dated 19th April, 1918, confirmed nationalization of artistic treasures housed in the residence of the former Grand Duke, Nicholas Konstantinivitch (Romanoff), in Tashkent. This nationalization was declared after the February Revolution of 1917. Enactment 173 of the CPC of the Turkistan Republic, dated 31st July, 1921, banned treasure-hunting and amateur arbitrary excavations. Decree 177 of the same date banned exportation and selling of "artistic and antique articles abroad". Decree 178, also enacted on 31st July, 1921, stipulated "registration, accounting and protection of artistic and ancient monuments in possession of private persons and societies in the Turkistan Republic".

Hand in hand with setting up of foundations of state legislation on protection of monuments came the establishment of bodies called to practically realize these Decrees and Enactments. At the beginning, in 1918-1920, such bodies organized like more or less representative commissions were established either on the initiative of local lore experts or by deci-

sion of local-municipal, regional or military authorities.

Thus, in the autumn of 1918, the former members of the TALC, V.L.Vyatkin and B.N.Kastalsky along with the local architect, M.F.Maurer, having noted the ever-increasing catastrophic leaning of one of the fifteenth century Samarkand minarets (Ulugbek's madrasah), formed a commission to save it and their efforts were supported by the City Council of Samarkand.

In 1919 another commission headed by artist A.K. Tatevosyan was also set up in Samarkand.

A year later, when Bokhara insurrectionists together with the Red Army seized Bokhara, the Representative of the revolutionary troops called V.L.Vyatkin from Samarkand by telegraph to register ancient manuscripts and other cultural valuables abandoned by the Emir and his retinue who had fled to Afghanistan as well as to ascertain the most valuable architectural monuments.

These and other commissions similar to them, undoubtedly, played a positive role in conservation of Central-Asian ancient monuments in the heat of the stormy military and political events of 1918-1920. However, the establishment of a permanent, solid governmental body was within power of only the Turkistan Republican administration. The initiative of setting up such a body came from the Commission of the All-Russia Central Executive Committee (ARCEC) on Turkistan. Outstanding functionaries of the Bolshevik party and the Soviet State, V.V.Kuibyshev, Ya.E.Rudzutak, M.V.Frunze, Sh.Z.Eliava, joined the Commission. The Turkistan Commission of ARCEC authorized its proxy, the Chief Director of the Central Department of Archives (CDA), D.I.Nechkin, "to organise protection

of ancient and artistic monuments in Turkistan", while at the early stages Decree 191 of Turkistan Republican CEC, dated 31st January, 1920, made the CDA responsible for protection of "all historical monuments of science and art in Turkistan" as well as for "undertaking archaeological research and collection of various scientific, literary and artistic materials for proper examination". In May, 1920, an ad hoc Commission headed by D.I.Nechkin set off "to inspect ancient artistic monuments in Samarkand and to take measures for their protection". As a result, the Chief Director of CDA decided to establish the standing Samarkand Commission for protection and restoration of ancient and artistic monuments ("Samcomstaris") on July 1st to be headed by V.L.Vyatkin. This Commission became the first nucleus of the Committee on Museums and Protection of ancient, artistic and natural monuments (Turcomstaris).

In accordance with Decree 127 of the Turkistan Republican CPC, dated 23rd May, 1921, the Committee was established "for uniting and managing all the museum work as well as for protection and restoration of monuments of antiquity, art and nature". The Decree stipulated that "the management of Turcomstaris is based in Tashkent; while realization of tasks locally is arranged through the bodies set up by the head organ, through provisional or standing Commissions, as well as by way of scientific expeditions and delegating special emissaries". It was emphasized that "all regulations and undertakings of Turcomstaris providing the state museum fund and protection of ancient, artistic and natural monuments... were compulsory to all local authorities".

Governmental importance of Turcomstaris's activities and the incorporated Samarkand Commission's was reiterated by Enactment 151 of the Turkistan Republican CPC, dated 26th June, 1921, according to which their efforts in conservation of ancient monuments were recognized as "extraordinary and extremely urgent", as well as by CEC and CPC Decree 70, dated 5th May, 1923, confirming that repairs and restoration of architectural monuments could be undertaken only by Turcomstaris or its bodies locally.

Turcomstaris existed up to the time of fixing national boundaries in Central Asia, i.e. the time of creation (instead of Turkrepublic, Bokhara and Khoresm People's Republics) of Union and Autonomous Soviet Socialist Republics and Autonomous Regions - Uzbek, Turkmen, Tadzhik, Kazakh and Kirghiz.

In 1921-1924 Turcomstaris accomplished 18 various expeditions and tours, actively cooperated with other scientific establishments of not only Central Asia but also Petrograd and Moscow, undertook measures to set up apart from the Samarkand Commission other commissions and societies of antiquity-lovers, "mainly among indigenous population" to provide direct protection of monuments, "in places of highest concentration of ancient monuments". Such a commission was set up in 1924 in Ferghana, similar bodies were planned to set up in Bokhara, Ashkhabad, Merve, Frunze and other places.

In compliance with the materials prepared by Turcomstars, the CEC and CPC of the Turkrepublic (Enactment 52 of 27th March, 1924) over 30 historical and archaeological monuments, including all major architectural monuments of Samarkand, Uzghen, Kokan-

da, Tashkent and the site of the ancient township of Afrasiab (Samarkand), the Old Merv and Nissa (in Turkmenistan), Akh-Peshin (in Kirghizia), etc., were registered and taken under state protection (a year later there were already 72 ancient monuments on the list).

Turcomstaris also endeavoured towards repair and restoration of structures in greater need of renovation. Because of limited capital one had to choose the most valuable things from the point of view of their historical, cultural and artistic importance in preference to others and this, in its turn, required a more thorough examination of them. Therefore, state registration of many of them frequently went along with their photofixation and detailed scientific description, while for the fullest examination of some buildings in Samarkand archaeological investigations of underground basements were carried out for the first time in Central Asia. Thus, in 1920 the original base of the Ulugbek's madrasah and the level of Registan square in the XV-XVII centuries were discovered; in 1922 the foundation of one of the mausoleums of the famous Shahi-Zinda necropolis was examined, while in 1924 archaeological and architectural examination of Timur-Gur-Emir's tomb was undertaken.

As a result of all these efforts conservation conditions in which some architectural monuments were preserved happened to be determined and recommendations on their repair and restoration were elaborated. Many fourteenth-seventeenth century buildings in Samarkand and some buildings in Bokhara and other towns were repaired (roof and dome mending, cleaning and fixing fragments of tile facing, etc.).

Repairs were the major type of conservation and

restoration activities of Turcomstaris not only due to financial handicaps but also because of the fact that the Committee's administration clearly realized its unreadiness at that time for restoration ("material rehabilitation of former shapes") of architectural monuments of Central Asia bearing in mind both want of restoration personnel and lack of knowledge embracing history of building technology, equipment and other problems of history and archaeology. Dwelling on restoration of architectural monuments in Central Asia D.I.Nechkin pointed out that "it was out of the question at the time, to say nothing of the fact that even strictly-ruled restoration lessens the archaeological (i.e. historical and cultural, - B.S.) value of the monument concerned". This, quite understandable in our time, careful approach to rehabilitation of ancient architectural monuments prevailed, in particular, when solving the problem of the aforesaid "leaning minaret" of the Ulugbek's madrasah in Samarkand. The chief of operations, M.F.Maurer, opposing the suggestion of dismantling the leaning minaret brick by brick and subsequently doing the brickwork anew, said that "after restoration" in this manner "the ancient monument would be actually destroyed while in its place a "novelty" would come into view with no scientific meaning and maybe hideous in execution".

Realizing the complexity of restoration Turcomstaris did not keep clear of its possible undertaking in those cases when it seemed scientifically valid and endeavoured its accomplishment. Planning to renew in due time the missing fragments of tile decoration of the fifteenth-seventeenth century structures the Samarkand Commission set as early as in 1921-1922 to

close studies of glazed wall tile engineering and technology; the studies were mutually conducted by V.L. Vyatkin and local craftsmen under the guidance of the oldest among them, Abdu-Kadyr Abdu-Bakiev.

Museum work also held an important position in the activities of the administration of the Turkrepublic and Turomstaris. In 1918-1924 four small old museums were reorganized and considerably increased in size: the Principal Turkistan Museum in Tashkent, the Regional Museum in Samarkand, the Ashkhabad and Ferghana Museums. New state museums were opened: the Central Artistic Museum in Tashkent, the Namangan Municipal Museum of local lore, the Khorezm Museum of History and Revolution. The expansion of the old museums and the establishment of the new ones became possible owing to the transfer of nationalized private collections (for example, the collection of the former Grand Duke, Nicholas Konstantinovitch) to them, allocation of considerable capital for acquisition of single articles and collections inflow of exhibits from different exhibitions and scientific exploration parties as well as receiving artistic and other museum valuables from the Central Museum Fund of Russia.

The development of expository arrangements in recent years raised the problem of restoration of museum valuables. And if ceramics used to be simply glued in museums and at exhibitions the way it had been done before, the display of a gypsum panel fretwork from a Medieval palace on the Samarkand Regional Exhibition required application of new restoration techniques. The fragments of a gorgeously ornamented panel were discovered for the first time in 1913 during the excavations of V.L.Vyatkin at the

site of the ancient township of Afrasiab. In 1919 it was decided to go on with the excavations so that to extract materials for the "scientific section" of the Exhibition. V.L.Vyatkin's student, M.E.Masson and painter-restorer M.V.Stolyarov not only discovered a room with the fretted panel but also removed this panel (fragment by fragment) from the walls, brought it to the Museum and restored large panels for the display at the Exhibition. It is worthy of notice that the panel's restoration was carried out without any "newly-made additions".

As a whole, the years 1917-1924 proved to be an important stage in the formation of state protection and restoration of Central-Asian cultural and artistic monuments.

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AU SUJET DES PRINCIPES THEORIQUES DE
RESTAURATION DES OEUVRES DE LA PEINTURE
D'ICONES RUSSES ANCIENNES, ADOPTES EN
URSS

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Zagreb 1978

AU SUJET DES PRINCIPES THEORIQUES DE LA RESTAURATION DES
OEUVRES DE LA PEINTURE D'ICONES RUSSES ANCIENNES, ADOPTES
EN URSS

I.P. Gorine

Les principes théoriques de restauration des oeuvres d'art ont pris actuellement une importance particulière dans la tâche principale - la protection et l'étude du patrimoine artistique.

Malheureusement, malgré le réseau développé des organisations de restauration en URSS, malgré l'existence des cadres de spécialistes, occupés à la résolution des problèmes méthodiques de la conservation pratique, ce n'est qu'un nombre limité de spécialistes, qui s'occupent de l'élaboration des principes théoriques de restauration des oeuvres d'art. En ce qui concerne la tentative de généraliser ces principes pour toutes les oeuvres d'art et de culture mobilières, on vient juste de l'entreprendre.

Dans la pratique de restauration de tous les jours ce problème est résolu par le Conseil de restauration⁽¹⁾ en fonction de chaque oeuvre concrète, fût-ce un tableau une peinture murale, une sculpture, un objet d'archéologie, etc.

⁽¹⁾Le Conseil (ou la Commission) de restauration - c'est un organisme de contrôle, adopté en URSS depuis 1918 pour surveiller l'exécution des travaux de restauration. Il approuve la tâche de la restauration, contrôle périodiquement la marche des travaux, apporte des correctifs, admet l'oeuvre après la restauration. En règle générale le Conseil de restauration est composé de restaurateurs, peintres, historiens d'art, conservateurs qualifiés.

Les principes théoriques de la restauration, et plus précisément, de l'enlèvement des repeints et de la reconstruction sont élaborés mieux par rapport à la peinture russe ancienne (peinture d'icônes). Cela se conçoit. L'icône, comme un objet de culte, destinée à l'admiration, à l'affermissement des églises, des maisons a fait l'objet de réparations,^{de} transformations et de repentirs plus que les autres peintures (à l'exception des frêscues)

La tâche de rendre à une oeuvre son aspect d'origine devenue une nécessité évidente à la limite du XX siècle, a exigé l'élaboration des principes théoriques précis de restauration des icônes. Cela a été nécessaire d'une part parceque l'histoire d'art n'avait presque pas une seule oeuvre authentique, et d'autre part, parceque les peintres d'icônes continuaient à pratiquer le repentir.

Pour la première fois les principes théoriques de restauration des oeuvres de la peinture russe ancienne ont été mis au point et formulés nettement en République soviétique à la limite des années 1920 par la Commission de Russie pour les affaires de restauration auprès du Département de musée du Commissariat du Peuple de l'Instruction. I.E.Grabar, Président de cette Commission, peintre et un des plus grand historien d'art, a pris une part active à l'élaboration de ces principes.

Il a été recommandé aux restaurateurs de consolider les oeuvres de la peinture d'icônes et de leur rendre l'état original par voie du dégagement par couches (enlèvement) des peintures récentes (repeints). Mais si les procédés de la consolidation et du dégagement ne présentaient pas de problèmes, les méthodes de restauration des lacunes sur la surface des oeuvres d'art exigeaient une étude approfondie et une révision. Sur cette voie, comme supposait alors et à juste titre I.E.Grabar, les restaurateurs se trouveront devant un labyrinthe, où l'on peut facilement s'égarer.

Comme on sait, les maîtres des époques passées se

permettaient les choses impossibles: ils ajoutaient les figures entières, restauraient les compositions d'après les fragments restés intacts, refaisaient la peinture à nouveau. Les pertes irrévocables des oeuvres d'art russe ancien causées par ces interventions sont incalculables. C'est pourquoi la Commission pour les affaires de restauration au nom de la vérité historique et artistique des oeuvres de la peinture russe ancienne a strictement interdit les interventions basées sur les goûts subjectifs et suppositions arbitraires, s'est déclarée contre les apports et les reconstructions sur les oeuvres elles-mêmes. On a adopté la méthode de neutralisation des lacunes sur la peinture par un ton neutre. Les icônes de A.Roublev de l'église "Ouspénié" de la ville de Zvenigorod, actuellement à la Galerie Tretyakov, peuvent servir d'un exemple brillant de cette décision.

Ces principes fondamentaux étaient alors à la base de la pratique de l'Atelier central de restauration (CGRM) créé en 1924. Ces principes ont été étendus également sur les secteurs de restauration créés alors auprès des musées et sur les organisations de restauration indépendantes, se trouvant dans les centres de concentration des oeuvres d'art russe ancienne.

Au cours de la période écoulée du développement et du perfectionnement des méthodes soviétiques de restauration, les principes adoptés dans les années 1920 ont subi certains changements. Tout en se développant, ils n'ont pas été précisés pendant les forums élargis des spécialistes jusqu'à 1968, si on ne tient pas compte de quelques publications et exposés; ils n'ont pas été approuvés par les résolutions des conférences de toute l'Union Soviétique.

Comme résultat, les point de vue différents sur le problème de la reconstitution de l'aspect d'origine des oeuvres d'art ont commencé à se manifester dans les organisations de restaurations principales du pays. Ces diffé-

rences ont été conditionnées d'un côté par l'utilisation différente de l'oeuvre d'art - par les exigences de l'exposition ou bien de l'étude historique et artistique de l'objet, et d'un autre côté, elles ont été fondées sur le prestige des anciens maîtres, et comme conséquence, sur les traditions qui se sont formées dans telle ou telle organisation.

Une large échange d'opinions est devenue nécessaire et cette échange a eu lieu à la Conférence de l'Union Soviétique de 1968 sur les principes de restauration des oeuvres de la peinture russe ancienne (peinture d'icônes). Plus de deux cents spécialistes - représentants des Instituts de l'histoire d'art, des organisations de restauration et des musées de Moscou, de Léninegrad, de Novgorod, de Vladimir, de Iaroslavl, des capitales et des villes des Républiques fédérées ont pris part à cette conférence

La conférence a constaté alors que malgré le progrès dans l'élaboration des principes théoriques et des méthodes de restauration des icônes, le problème de restauration de l'oeuvre d'art, et en particulier l'attitude du restaurateur envers les principes d'utilisation des reprints, le rapport réciproque avec la peinture de l'auteur, le problème de la mise sur ton, l'admission des reconstructions ne sont pas complètement résolus théoriquement, et pratiquement ils se basent sur les traditions différentes et souvent sur les goûts subjectifs.

Après une large échange d'opinions la conférence a recommandé les principes uniques de restauration de la peinture russe ancienne, obligatoires pour toutes les organisations de restauration et tous les restaurateurs de l'Union Soviétique. Dans le fond même ils sont basés sur les principes de conservation, de dégagement et de restauration des oeuvres de la peinture russe ancienne, adoptés dans les années 20 par la Commission de Russie pour les affaires de restauration en tenant compte et en utilisant l'expérience acquise pendant une période demi-séculaire

des travaux pratiques.

On a appelé cette période à juste titre "une période des découvertes", car elle a enrichi l'histoire de l'art russe-soviétique par des milliers d'oeuvres de haute qualité artistique, inconnues auparavant, par des noms des peintres éminents, elle a aidé à révéler et à définir les écoles et les ateliers locaux.

En tenant compte de tout cela, l'auteur a pensé utile de mettre au courant ce forum international du Comité pour la conservation des principes théoriques de restauration de la peinture en détrempe de chevalet (peinture d'icônes) adoptés aujourd'hui en URSS.

La restauration des oeuvres de la peinture russe ancienne (peinture d'icônes) a pour but l'enlèvement des couches de la peinture n'ayant pas de valeur propre et la conservation de ces oeuvres pour garantir leur intégrité à l'avenir. Au cours du dégagement des icônes on utilise, si c'est possible, les restes de la peinture ancienne dans les endroits où la peinture originale est perdue. La neutralisation par un ton neutre est admise. Les endroits mis sur ton, en règle générale sont discernables de la peinture d'auteur qui les entoure. Il n'est pas admissible dans une large pratique de faire la reconstruction des parties manquantes de l'original. Dans le cas d'endommagement d'une partie importante de l'image dont dépend entièrement l'expressivité artistique et émotionnelle de l'oeuvre, la décision sur la marche de la restauration est prise par une commission entredépartementale spécialement convoquée avec la participation des propriétaires de l'oeuvre et des historiens d'art. La restauration des parties manquantes de la peinture s'effectue uniquement dans ces cas exceptionnels sur la base du projet bien argumenté, présenté et approuvé par cette commission. Les matériaux et la manière d'exécution sont également discernables de la peinture de l'auteur. Au cours de la restauration de la peinture russe ancienne tous les travaux, dictés par la compréhension subjective, n'étant pas examinés par cette commission, sont interdits.

Le dégagement des oeuvres de la peinture russe ancienne ayant plusieurs repeints, si le détachement ou la transposition sont impossibles, est effectué couche par couche avec un examen détaillé, une description et une fixation photographique de chaque couche. Si quelque repeint présente un intérêt historique ou une grande valeur artistique, les travaux de dégagement sont interrompus jusqu'à la convocation de la commission spéciale et la prise de décision. Le dégagement est effectué conformément à la technologie généralement admise.

La restauration des icônes dans les musées locaux ayant de petites laboratoires est fait sous la surveillance des spécialistes envoyés périodiquement en mission par les institutions centrales. Les icônes dégagées sont acceptées elles aussi par une commission, composée de représentants de ces institutions (deux restaurateurs de la qualification supérieure au moins). La commission a le droit de donner les ordres d'exécution pour les travaux ultérieurs; cela est rédigé dans les comptes rendus. Pour chaque travail concret la commission conserve le personnel constant. Les présidents des commissions rendent périodiquement compte aux instances supérieures. Avant le commencement et au cours des travaux de restauration liés au dégagement de la peinture, on procède aux études scientifiques, physiques, chimiques et biologiques de l'oeuvre. Tous les travaux de restauration sont soigneusement documentés dans les passeports ayant la forme unique, adoptés pour les oeuvres d'histoire et de culture mobilières, aussi bien que dans les comptes rendus et tout le cycle des opérations de restauration est reflété dans le journal. La documentation photographique de la vue générale de l'oeuvre, des fragments les plus importants, faite avant le dégagement de l'icône, pendant ce processus et après la fin des travaux est jointe à ce passeport. Dans les cas particuliers on fait des calques avec l'indication de tous les endommagements se trouvant sur l'icône. On inscrit dans le passeport l'inventaire complet de documents joints.

Il est recommandé aux administrations des musées et des organisations de restauration d'introduire en large pratique la fixation objective de l'état des oeuvres à l'aide des méthodes d'examen physiques (rayons ultra-violet, infra-rouges, rayons X, etc.), des analyses chimiques et des méthodes d'examen biologiques.

Il faut cependant noter, que ce ne sont pas encore toutes les organisations de restauration qui ont permis les cadres des physiciens, des chimistes, des biologistes. Elles n'ont pas toutes également de laboratoires équipés à ces effets.

Certes, les principes de restauration des icônes, exposés plus haut, établis en URSS et ayant beaucoup de commun avec les principes adoptés dans les autres pays, ne sont pas un dogme. Les spécialistes comprennent fort bien que dans la pratique de restauration on a rarement affaire aux oeuvres semblables, chaque oeuvre demande une approche individuelle. De ce fait le schéma que nous venons d'exposer étant une instruction d'agir, en même temps peut admettre des écarts ou autres variantes dans la résolution des problèmes de restauration en fonction de chaque oeuvre. Dans tous les cas il est important de conserver l'authenticité historique et artistique de l'oeuvre.

Le rapport est accompagné par la projection des photos en couleur. Outre cela, il y aura un album de photographies illustrant les principes de restauration de l'icône russe ancienne.

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FROM THE HISTORY OF PROTECTION AND
RESTORATION OF CULTURAL MONUMENTS
IN THE TRANSCAUCASUS
(1st DECADE OF SOVIET POWER)

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5th Triennial Meeting
Zagreb, 1978

FROM THE HISTORY OF PROTECTION AND RESTORATION OF CULTURAL
MONUMENTS IN THE TRANSCAUCASUS (1st DECADE OF SOVIET POWER)

N.L. Podvigina

The territory of the Transcaucasian Soviet Socialist Republics is affluently covered with ancient monuments. Numerous ancient temples, monasteries, fortresses, cavern complexes, palaces, bridges, sites of ancient townships, burial grounds, etc. have been kept in existence up to now. Relics of Transcaucasian ancient times for a long time attracted the attention of scientists and antiquity - lovers among the forefront representatives of the Russian and local nobility and intellectuals.

Not a single museum existed in Azerbaijan before the establishment of Soviet power. The Echmiadzin monastery museum was the only Armenian centre to draw museum articles of value, mainly of ecclesiastical nature. The Caucasian Museum in Tiflis (now the State Museum of Georgia) founded in 1852 to house not only Georgian but also Armenian and Azerbaijanian relics of the past, ranked the largest in the Transcaucasus. The collection of the Kutaisi Society of History and Ethnography (now the Kutaisi Historical and Ethnographic Museum) founded in 1912 was quite noteworthy. Apart from these museums only private and public collections as well as art collections in possession of Church bodies existed in the Transcaucasus.

At the end of the nineteenth - beginning of the twentieth century the first efforts were exerted to protect relics of the ancient times. Small-scale repairing of architectural memorials began but it was

not done methodically. The majority of architectural structures lacked permanent supervision and care, some of them falling into decay catastrophically. There was no state legislature on protection of monuments in tsarist Russia while the efforts of archaeologists, enthusiasts of regional studies and antiquity - lovers were inadequate to keep cultural survivals of the past from destruction.

The situation was radically changed after the establishment of Soviet socialist republics in the Transcaucasus (Soviet power gained the victory in Azerbaijan in April, 1920, in Armenia in November, 1920, and in Georgia in February, 1921). In the very first years of Soviet power, being placed in the hardest circumstances possible when the major task was to rehabilitate national economy ruined by the Civil War and total devastation, the Governments of the Transcaucasian Republics, following suit of the RSFSR Government, started vigorous activity to protect cultural heritage.

Perceiving cultural heritage of mankind with critical apprehension bolsheviks strived to make use of it while creating socialist culture. To make the greatest cultural treasures, formerly in possession of the exploiter classes, accessible in their entirety to the working people a sizable effort was undertaken in the Transcaucasian Republics in the field of museum construction and protection of objects of scientific, historic and artistic value. Among the first measures taken by Soviet power in this direction were disestablishment of the church, nationalization of cultural institutions hitherto in possession of ecclesiastical organizations and declaration of all the properties of church and religious societies to become the people's property (Decrees of the Armenian Revolutionary Commi-

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ttee of December 10, 1920, and the Georgian Revolutionary Committee of April 15, 1921).

In November 1921, the Council of People's Commissars of Georgia approved the Resolution "On Utilization of Church-plate", thereby handing over the entire church property to local executive committees and placing it at their disposal. In January 1923, the Echmiadzin Museum was nationalized and placed under the authority of the People's Commissariat of Education of Armenia.

In the early 1920s, Republican Museums were established in the capital cities of Georgia, Armenia and Azerbaijan to become both scientific institutions and centres of studies in history and culture of the Transcaucasus. The State Museum of Georgia was set up on the basis of the Caucasian Museum in Tbilisi. In 1920, the Azerbaijan State Museum was established in Baku. The State Museum of Armenia was set up in Yerevan.

Apart from Republican museums the People's Commissariats of Education directed setting up of local lore and historical and art museums in different districts of Georgia, Armenia and Azerbaijan. The Governments of the Transcaucasian Republics gave extensive support to museums set up locally. Thus, in February 1922, the Revolutionary Committee of Georgia approved the "Resolution about the Mingrelian Museum at Zugdidi". Museum repositories were set up on the Armenian territory of Dvina, Taltin, in the Temples of Ripsime, Zvartnotz, at Nor-Bayazet, Oshakan and other places.

It was in the first years of Soviet power that the museum funds of the Transcaucasian Republics began to replenish their stock with exhibits from the museums of Russia and other Republics. The RSFSR Go-

vernment considered it necessary to preserve and return to the formerly oppressed peoples of tsarist Russia those relics of historic, artistic and cultural value which had been plundered before. To register memorials of ancient art carried off from Georgia after the introduction of the tsarist autocracy an ad hoc Commission was sent to Russia to result in bringing back to Georgia 308 manuscripts dating from the 9th century and many valuable articles that had been stored in Petrograd museums. In May 1923, museum collections and archives evacuated during the First World War (total of 14 railway cars) were returned to Georgia. Moscow and Kiev also sent a number of interesting museum exhibits to Georgia.

In November 1923, the Council of People's Commissars of Georgia approved the resolution "On Reorganization of Museum Work" on the basis of which the Natural and Historical Museum and the Historical and Ethnographical Museum of Georgia were established in the capital city of the Republic incorporating museum funds available in Tbilisi and valuable articles reevacuated from Russia.

In the early 1920s, the funds of the Armenian State Museum expanded on account of collections from the Echmiadzin Museum evacuated to Moscow during the First World War as well as on account of exhibits received from the Museum of the Lazarev's Institute in Moscow. Belongings and the Library of the Armenian Ethnographic Society's Museum of Tbilisi were also transported to Yerevan.

In January 1924, the Council of People's Commissars of Azerbaijan petitioned for the transfer of all Azerbaijanian museum valuable articles kept in Tbilisi, Moscow and Petrograd back to the Azerbaijan State Mu-

seum. In 1925, an Ad hoc Commission of experts went to Moscow and Leningrad to select and receive museum valuable articles associated with the history and culture of Azerbaijan. Soon after that Georgian, Armenian and Azerbaijanian museums received numerous paintings by Russian and West European artists, icons, sculpture, jewelry, porcelain, etc. from the Tretyakov Gallery, the Russian Museum and the Hermitage. All these facts provided evidence of a completely new national policy adopted by the young Soviet state as well as of a new relationship between the peoples of the former Russian Empire, a relationship based on equality and mutual respect for the history and culture of all the peoples concerned.

It was in the very first years of Soviet power that memorials of the ancient times came up to be regarded as the working people's national property. Care for cultural and historical values was recognized as an endeavour of state concern. Special committees were set up within the framework of the People's Commissariats of Education in every one of the three Transcaucasian Republics, henceforth to be entrusted with protection of survivals from the past and cultural memorials. In 1921, a Department of Museums and Monuments' Protection attached to the Georgian People's Commissariat of Education was set up to be followed two years later by a Committee on Protection of Antiquity and Art Memorials. At the same time, a Committee of Ancient Monuments and Art Values' Protection was established in Armenia. In 1923, the "Resolution about the Azerbaijan Archaeological Committee" charged with identical tasks was approved.

On December 18, 1923, the Council of People's Commissars of Armenia issued a Decree "On Protection

of Antiquity Memorials" emphasizing that all of them were "state property to be inviolable".

On March 4, 1924, the Council of People's Commissars of Azerbaijan adopted a Resolution "On Protection of Antiquity Memorials in the ASSR" and, a year later, an Addendum thereto indicating that "all finds, buried treasures and single articles of archaeological, historic and artistic value" accidentally discovered while making excavations, etc. were "subject to obligatory placing under the authority and at the disposal of the Armenian State Museum through the Azerbaijan Archaeological Committee". On June 4, 1924, a Resolution "On Protection of Ancient, Artistic and Natural Monuments" was issued by the Central Executive Committee of Georgia. The Decree of the All-Union Central Executive Committee and the RSFSR Council of People's Commissars "On Registration and Protection of Art, Antiquity and Nature Monuments", dated January 7, 1924, was the underlying principle of all the Resolutions above.

All these Governmental Resolutions proved with certainty that protection of cultural heritage in the Transcaucasian Republics had become the State's concern just like in the RSFSR. That was the way the foundations of Soviet state legislature on protection of historic, cultural and artistic monuments were set out.

Registration and cartography of monuments, their placing on Government record, ascertainment of the degree of their preservation, repairs and restoration in case of need and protection arrangements were the pacing directions of antiquity protection committees in the first decade of Soviet power. To this end, special expeditions were sent out by the committees to

different areas of the Republics. In 1925, an expedition of the Armenian Antiquity Protection Committee put on record monuments of the historic Lori. All the monuments were described, photographed and measured, lapidary inscriptions were also collected and printed out. In 1926-1928 similar expeditions did the same kind of work in the Sevan Region.

In 1924-1925, the Georgian Antiquity and Art Protection Committee sent a number of instructions to provinces outlining classification of architectural structures according to their artistic and historic importance and indicating considerations to be followed in abolishing churches and confiscating their property. The Abkhazian Scientific Society, founded in Sukhumi in 1922, started dealing energetically with problems of protecting cultural monuments on the Black Sea coast of the Caucasus. On January 7, 1925, an Ad hoc Commission on Protection of Records of the Past was set up in conformity with the Abkhazian Central Executive Committee's Resolution.

In 1924, the Azerbaijanian Archaeological Committee distributed monuments registration lists among district executive committees requesting them to collect necessary data. New facts were obtained as a result of this endeavour to supplement the available information about antiquities of Azerbaijan. In February 1927, permanent sections of the Archaeological Committee were set up in Nakhichevan and at the Karabakh Highlands following the Resolution of the ASSR People's Commissariat of Education.

All the committees engaged in protecting monuments relied in their activities on the assistance of Soviet authorities and local population. Committees' representatives from among local people of artistic occupation,

educationalists, Soviet and party functionaries successfully operated in many districts of these three Republics continually making it clear to the population that it was necessary to protect historical and cultural values now that they became working people's property. And these efforts immediately started to produce tangible results. Peasants, construction workers, and students came to museums and brought with them accidental finds which frequently turned out to be real museum pieces of value. People's interest in the history of their motherland came to light; historical and art museums as well as museums of regional studies received more public with every coming year.

In the twenties first steps were made towards monuments' protection at the sites of newly erected buildings. In 1926, the Azerbaijanian Archaeological Committee approached the "Azneft'" with a request to reach a consensus of opinion on oil drilling plans and to identify boundaries of oil fields expansion so that to take action in good time for protection of ancient objects located there.

At the same time first repairs and restoration of Transcaucasian architectural monuments started under the guidance of the Republican Committees responsible for monuments' protection. Funds were allocated to restore the Nakhichevan Tower - Mausoleum of 1186. In 1927-1928, small-scale repairs were undertaken to renovate the Baku fortification walls. It was at that time also that the "Azneft'" allocated funds to restore the Ramanin Castle of the 13th-15th centuries. In 1927, efforts exerted by the Azerbaijanian Archaeological Committee and the State Museum of Azerbaijan contributed to roof re-covering of the Nikhin Palace (end of 17th - beginning of 18th century). Wall paint-

ing restoration was envisaged at a later stage.

In 1928, following the instruction of the Georgian People's Commissariat of Education a special commission inspected the famous Mtshet Temple of Jwari endangered by a land-slide. Repairs of Jwari and a number of other large monuments in Georgia were undertaken at the end of the twenties and at the beginning of the thirties. On the Armenian territory partial repairs and restoration were carried out in the Temples of Ripsime and Zvartuotz, at Ahpata, Tsahkadzora and other places. Restoration of two monuments succeeded in complete renovation of a fifth-century basilica at Ereruike and a thirteenth-century bridge at Sanain. At the end of the twenties efforts were undertaken to save frescoes in the Church of St. Pogos and Petros in Yerevan, some of them dating back to the year 1131. Armenian painters hand in hand with G.O. Chirkov, one of the best restorers in this country, invited from Moscow tried hard to remove the frescoes for 45 days but failed to do so since they were far too brittle. The efforts, therefore, were bound to stay within the limits of in situ examination.

As a whole, in 1920-1930 a sizable effort was undertaken in the Soviet Transcaucasian Republics to protect records of the past. Foundations of state legislature on protection of cultural monuments were laid and a lot was done to reorganize museum work, the major part of ancient survivals was systematized and collection of works of art began to be distinguished by scientific, purposeful nature. A new step was envisaged towards elaboration of scientific methods of research within the scope of cultural monuments' restoration and safe-keeping of valuable museum objects.



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LA RESTAURATION DES TABLEAUX DES
GALERIES A FLORENCE AU XVIIIème
ET XIXème SIECLE

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LA RESTAURATION DES TABLEAUX DES GALERIES A FLORENCE AU
XVIIIÈME ET XIXÈME SIÈCLE

Gabriella Incerpi

Dans les Archives des Galeries de Florence il y a beaucoup de documents relatifs à la restauration des tableaux des Uffizi et du Palais Pitti au XVIIIème et XIXème siècle.

J'y ai trouvé des listes de tableaux avec l'indication des interventions subies, des factures et aussi des rapports détaillés sur les méthodes suivies.

En 1764 Pietro Leopoldo avait chargé un restaurateur de la conservation des peintures des Uffizi. Mais les peintres employés pendant le XVIIIème siècle pour cette tâche n'étaient pas des spécialistes et leur œuvre était limitée "al solo oggetto della meccanica operazione di risarcire e rinfrescare qualche quadro danneggiato". 1)

Cette opération consistait à nettoyer les tableaux avec de l'eau et leur donner après une couche d'huile de pavet.

"Prendere acqua chiara -on peut lire dans les procès verbaux- e con spugna diligentemente lavare [il quadro], di poi asciutto prendere dell'olio di papavero, e stenderlo, di poi levarlo a fine di vedere di terre almeno in parte de lo sudicio e macchie che ivi si trova".

Les professeurs de l'Accadémie des Beaux Arts, qui dirigeaient ces opérations, étaient très méfiants envers toute méthode de nettoyage et recommandaient toujours "di non far uso di corrosivi né di vernici" mais simplement "se resterà macchie o potture operare diligentemente col colore". 2) Pour cette raison les tableaux des Galeries florentines étaient, à la fin du XVIIIème siècle très sombres, arides et couverts de repeints.

Une nouvelle organisation de la restauration des peintures se manifestait à Florence dès 1796.

Les œuvres d'art de la Galerie des Uffizi venaient d'être arrangées selon les principes modernes de classification historique et Tommaso Puccini, directeur du musée dès 1793, appelait un restaurateur toscan qui avait beaucoup travaillé à Rome, Vittorio Sampieri, pour nettoyer et vernir les tableaux plus fameux. Sampieri travailla

pour les Galeries de Florence jusqu'au 1827. "Invero egli fu -témoignent les documents- che introdusse fra noi i suoi sani metodi di restaurar le pitture". 3)

ORGANISATION

Tommaso Puccini, et les directeurs des Uffizi qui lui succédèrent, considéraient très important avoir les restaurateurs plus abiles du temps et les employer de façon stable à la conservation des tableaux du musée.

"Due sono a parer mio gli oggetti da aversi in mira per assicurare la stabile conservazione dei quadri -écrivait en 1823 le Sous-Directeur des Uffizi, Antonio de Montalvo, au Prince de Saxe, qui lui avait posé des questions sur la restauration des tableaux de Dresde- il primo è il riparare ai danni già avvenuti, il secondo è d'impe- dire che ne sopraggiungano per l'avvenire". 4)

Restauration, conservation, manutention sont les mots plus usés dans les documents de ces années.

Dans la 1ère moitié du XIXème siècle il y avait à Florence un "Primo Restauratore", chargé de la conservation des tableaux des Uffizi, un "Secondo Restauratore" qui s'occupait de ceux du Palais Pitti et des Palais Royaux, et un "Aiuto-Restauratore". Dès 1829 les restaurateurs des Galeries travaillaient aussi pour la Galerie de l'Académie des Beaux Arts.

On essayait surtout de garder les peintures dans un bon état de conservation, en assurant les meilleures conditions possibles de chaleur, humidité, lumière. Il faut dire qu'à Florence il n'y avait pas les problèmes du smog, que les chauffages à charbon produisaient à Londres et dans les villes du nord, mais qu'aux Uffizi il y avait une chaleur excessive pendant l'été. 5)

Montalvo écrivait à ce sujet que le principal moyen pour conserver en bon état les tableaux était "di non lasciarli troppo inaridire, ma di rinfrescarli e rivernicigli opportunamente... e di apprestare pronto riparo nel suo principio a qualunque degradazione che potesse riaffacciarsi".

I "Custodi della Galleria", c'est-à-dire les Inspecteurs responsables des Uffizi, étaient chargés d'attirer l'attention du Directeur sur les peintures qui manifestaient des inconvénients. Si l'état du tableau demandait plus qu'une simple opération de manutention, ou il s'agissait d'une oeuvre "di Primo Ordine", une Commission de professeurs de l'Académie des Beaux Arts examinait, avec le directeur et les restaurateurs, la

peinture et indiquait, dans un procès verbal, la méthode à suivre pour la restauration. La même Commission signait la relation finale de l'intervention.

"Per quante si voglia supporre intelligentissimo e diligentissimo il Restauratore -precisait Montalvo- non sarà mai troppa la sorveglianza di qualche Professore, per tenergli a freno la mano".

NETTOYAGE

"Convorrà avere grandissima attenzione -écrivait encore le Sous-Directeur des Uffizi- perchè il Restauratore sia estremamente circospetto e parco in ciò che riguarda la pulitura dei quadri, non pretendendo a farli ritornare nella primitiva nettezza, ma contentandosi di lasciar sopra quella patina, e quel grado di sporcizia, che non si può assolutamente tor via, senza attaccare le velature originali, specialmente nelle parti scure". 6)

Vittorio Sampieri, qui en 1796 avait vaincu la méfiance des professeurs florentins envers les solvants, était très prudent. Les factures indiquent qu'il nettoyait les tableaux avec un mélange d'esprit-de-vin et huile de té-rébenthène, la "mista" très commune en Italie au XVIII^e siècle.

Deux fois j'ai trouvé employée l' "acqua maestra", un produit de la soude, mais généralement les restaurateurs florentins préféraient la "mista" et l'aide mécanique du bistouri pour éliminer les repeints plus résistants et la crasse "che restasse internata nei pori della tela". 7)

RENTOILAGE

Montalvo écrivait que le premier devoir du restaurateur était de "assicurare bene la pittura, rintelandola ove occorra, spianando le screpolature, fissando il colore ove minaccia di scrostarsi e cadere ed altre simili cose". Mais le rentoilage était généralement considéré "una operazione materiale" et confié à des ouvriers ou des rentoilleurs externes à l'administration.

Francesco Acciai seulement, qui travailla aux Galeries de 1829 à 1865, exécutait souvent des rentoilages. La colle, à Florence, était composée de "Libbre 1 di Colla Tdesca e libbre 6 di Fiore di Farina per braccio 6 di tela". Du fiel et du miel étaient quelque fois unis au mélange. 8)

PARQUET COULISSANT

Le parquet coulissant, composé de "regoli longitudinali a coda di rondine incollati nelle committiture delle tavole, e da una intelaiatura di correntini in croce adattati in modo da tenere in guida le assi medesime perohè non si possano torcere, senza però impedire la naturale dilatazione e il restringimento del legname nelle diverse stagioni" avait été introduit en Toscane par Pietro Rombergh "legnaiolo tedesco" et fut adopté dès 1830 pour les grands tableaux sur bois des Galeries. 9)

TRANSPOSITION

Deux restaurateurs français, Barthelemy Marcon en 1806, et Marie Barret en 1807, proposaient leur méthode de trasposition au Gouvernement de la Toscane, mais les professeurs de l'Academie de Beaux Arts et le Directeur des Uffizi s'opposaient toujours à cette operation.

En 1837 Antonio Vannucci de Pistoia, IO) transposait de la toile sur toile un tableau de S. Maria dell'Umiltà, mais il était presque perdu et "non suscettibile d'altro modo di restauro". II)

En 1864 seulement, Secco-Suardo effectuait des transpositions de tableaux des dépôt des Galeries, pendant son Cours de Restauration organisé par le Gouvernement italien, mais les florentins considéraient toujours "che non doveva persi in opera che in casi specialissimi. I2)

RESTAURATION PICTURALE

Jusqu'à la fin du XVIIIème siècle les restaurateurs des Galeries étaient occupés à couvrir de repeints les taches des anciennes restaurations que le simple nettoyage avec de l'eau ou de l'huile de pavot ne pouvait effacer. Ces repeints, exécutés avec des couleurs huileuses, s'altéraient très rapidement et, après quelque années, il était nécessaire d'effectuer d'autres retouches. "I quadri di queste Regie Gallerie -scrivait Giovanni degli Alessandri, qui succeda à Puccini dans la direction des Uffizi- posson dirsi più maltrattati dalla imperizia di questi artefici, che non lo siano dal tempo; di modo che il più che resti da fare agli odierni restauratori sia di togliere dai quadri quello che vi fecero sopra i passati". I3)

Vittorio Sampieri introduisait à Florence, en 1796, les couleurs au vernis, donnant beaucoup plus de stabi-

lité aux retouches. Les restaurations modernes ont révélé que les restaurateurs florentins du XIXème siècle exécutaient des repeints au vernis très habiles, mais souvent très étendus.

VERNIS

Philippe Hackert avait proposé en 1778 au directeur des Uffizi, Giuseppe Pelli, le vernis "mastic", composé de résine mastio dissoute dans l'essence de térébenthine, mais il fut adopté pour les tableaux des Galeries seulement à partir de 1796.

Durant la même époque, le blanc d'oeuf était employé pour "refraîchir" les peintures sur bois. 14)

À la moitié du XIXème siècle le vernis "mastic" était souvent remplacé avec le vernis Damar, moins cher. À Florence on n'employait pas de vernis huileux, mais quelques fois des couches huileuses ou un mélange de cire et camphre était mis sur le dos des tableaux "per salvarli dalle tarme". 15)

FORMATION DES RESTAURATEURS

Il n'y avait pas une école de restauration. Dans la 1ère moitié du XIXème siècle un jeune peintre était choisi pour être "Apprendista-Restauratore". Il travaillait quelques années avec les restaurateurs des Galeries et après un long apprentissage pouvait aspirer à la place de "Aiuto-Restauratore". Mais cette méthode ne fut pas suivie de succès: quelque fois le jeune restaurateur préférait l'activité privée à l'emploi des Galeries, d'autres fois le directeur ne le jugeait pas assez capable pour être employé de façon stable. 16)

Les années qui suivirent on préférait pour cela, nommer un restaurateur déjà connu et habile à la place de "Aiuto-restauratore".

On peut dire, pour conclure, que les restaurateurs florentins employaient des méthodes simples mais assez propres et qu'ils avaient surtout le mérite de bien soigner les tableaux avec une manutention constante. Cette conception de la conservation évitait qu'il fallut avoir recours aux remèdes drastiques et souvent dangereux qui, à Florence aussi, étaient employés dans la restauration des tableaux privés.

Malheureusement cette tradition finit après l'Unité. Le Gouvernement italien ne jugeait pas nécessaire, à la

mort du dernier restaurateur nommé par le Granduc, de conserver l'emploi de "Restauratore delle Regie Gallerie".

-
- I) Archivio della Soprintendenza alle Gallerie di Firenze - XX, 1787, N°17 -
 - 2) A.S.G.F. - XX, 1787, N°37 -
 - 3) A.S.G.F. - XXVIII, 1796-97, N°53; ibidem, II, 1827, N°14 -
 - 4) "Sulla conservazione dei quadri delle pubbliche Gallerie. Parere richiesto dal Principe Federigo Augusto di Sassonia al Montalvi". A.S.G.F., XLVII, 1823, 19bis. Antonio Ramirez de Montalvo fut "Conservatore dei Regi Palazzi" de 1824 à 1828, Directeur des Uffizi de 1828 à 1849.
 - 5) "Interpellazione del Governo Inglese sui sistemi praticati nella Galleria e che tendono alla migliore conservazione delle pitture che in essa si custodiscono" A.S.G.F., LXXIV, 1850, N°37 -
 - 6) A.S.G.F., doc. cit. -
 - 7) "Nota di spese della R. Galleria" de 1813 à 1843,
 - 8) A.S.G.F., XXXVIII-LXXI; "Conservazione dei R. Palazzi e Ville", A.S.G.F. I, 1824-27, N°122 -
 - 9) A.S.G.F., LIV, 1830, I°, N°26; "Cons. Regi Palazzi", 1830-31, N°51, 1832-34, N°8 -
 - 10) A.S.G.F., XXXIII, 1806-1807, N°21; Archivio Accademia di Belle Arti, K, 1807-1808, N°19 -
 - II) A.S.G.F., 1837, LXI, N°29 -
 - 12) A.S.G.F., "Galleria delle Statue e Palatina", 1864, II, N°64 -
 - 13) A.S.G.F., LI, 1827, N°14 -
 - 14) A.S.G.F., XI, 1778, N°60 -
 - 15) Cfr. nota 7)-8) -
 - 16) A.S.G.F., XXXII, 1804-1805, N°8; XXXV, 1809, N°10 -

CARE OF WORKS OF ART IN TRANSIT

Coordinator : N. Stolow (Canada)

Assistant coordinator:

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 J. Cama Villafranca (Mexico)
 P. Cannon-Brookes (U.K.)
 E.K. Krollau (USSR)
 T. Morita (Japan)
 G. Rogers (Canada)
 K. Toishi (Japan)

Programme 1975-1978

1. Packing systems in use in various countries; questionnaire and evaluations.
 Survey of industrial packing systems internationally (Stolow and working group members).
2. Descriptive booklet, or report, with illustrations on packing methods for exhibitions, to be used by directors, curators, and museum administrators (Stolow, Rogers, Cannon-Brookes, Morita, Cadorin, Cama Villafranca).
3. Design and evaluation of recording devices to measure internal conditions of cases used in international exhibitions (Rogers, Toishi, Krollau).
4. Preparation of technical specifications for international exhibitions - with Committee on Exhibitions (ICOM) and Ad Hoc Committee on Insurance (ICOM) (Stolow, Cannon-Brookes).
5. Condition reports and reporting methods for exhibitions employing rational and universal descriptive terms (Stolow, Cama Villafranca).



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PROTECTION OF WORKS OF ART BY ENVELOPMENT

L.A. Kuzmitch and A.A. Zaitsev

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

PROTECTION OF WORKS OF ART BY ENVELOPMENT

L.A. Kuzmitch and A.A. ZaitsevAbstract

In museum practice instances of exhibiting paintings in galleries with instable relative humidity of air, varying from 30 to 40%, are frequent. Such variations produce harmful effects on the materials of the paintings and their supports. The only method for protection is the enveloping of paintings while on exhibit.

The investigations carried out make it possible to recommend polymethylmethacrylate (PMMA) plastic glazing and polyethyleneterephthalate (PETPh) film for enveloping. PMMA has a number of advantages compared to ordinary glass - it has a great resistance to blows and shocks. It is used here for protecting the front of the painting. The PETPh film has good physico-mechanical properties, heat resistance and wet-strength and is recommended for protection of the back of the painting.

The technology of manufacturing envelopes is simple, and is done in two stages.

The resulting envelope has not only protective properties, but is transparent. This provides for checking the preservation of works of art during their exhibition and transportation allowing for visual checking and also permitting measurement.

It is not rare in museum practice when paintings are exhibited in galleries characterized by unsteady relative humidity, temperature drops and ambient air pollution. The effect of these damaging factors, acting jointly or separately, leads to irreversible changes in painting materials. The only protection in such cases is envelopment of the works of art. Continuous investigations are underway in this direction carried out by our Laboratory's personnel.

Advances in chemical industry have brought about new materials satisfying all the requirements which can be fulfilled by packing materials. The Report now offered gives a description of the assembly and disassembly of an envelope made of plastic glazing and polyethyleneterephthalate film to cover the paintings.

1. Materials applied in producing an envelope.

It is well-known that plastic glazing has an advantage over simple glass - its resistance to impacts and shaking to occur during transportation.

To manufacture an envelope a plastic sheet polymethylmethacrylate (plexiglas) of LPT grade was used. Such plastic glazing possesses the following properties:

- specific impact resilience, Kg. force cm/cm^2 - 13 to 15;
- cross-breaking strength, kg. force cm/cm^2 - 1200;
- Brinell hardness, kg. force cm^2 - 17.5;
- Martens yield temperature, $^{\circ}\text{C}$ - 85-90.

Polyethyleneterephthalate film is made of polyethyleneterephthalate which is a product of polycondensation of dimethylterephthalate and ethylene glycol. Such a film is dense, transparent and flexible with a glossy surface and good mechanical strength in a wide range of temperatures and good dielectric properties. It retains these properties, due to its insignificant hygroscopicity, under the conditions of increased humidity. Very low gas permeability as well as grease- and oil-proofing properties and chemical stability made this film a valuable packing material.

Physical properties of the film:

- | | |
|--|------------------------------|
| - water absorption, % | 0.5 |
| - melting temperature, $^{\circ}\text{C}$ | 260 |
| - moisture permeability at 38 $^{\circ}\text{C}$ and 90% relative humidity (thickness of 25 g/cm^2) | 30 |
| - inflammability | catches fire which dies out |
| - cold resistance | remains elastic till minus 6 |

The film has identical mechanical properties in all directions.

2. Assembling and disassembling of an envelope.

An envelope has a form of a parallelepiped with one of its bases being the plastic glazing and the other one - polyethyleneterephthalate film. Both "bases" are equal in area to the area of a picture to be covered. When enveloped the picture is placed with its face side to the plastic glazing.

Both "bases" of the envelope are connected by a strip of polyethyleneterephthalate film along the entire perimeter. The width of such a strip equals the picture's thickness. The connection is made secure by adhering with polyester resin. This kind of adhesive guarantees a composite glue line fastening the film not only on the film but also plexiglas. The glued surfaces are superimposed after air drying and are pressed by a warm iron heated in the water bath.

Disassembling of an envelope (in case of need) is to be performed along the film-to-film joining line. The glue line is easily destroyed if wetted by formal - glycol and when a small disintegrating force is applied the films are separated. The film, however, remains undamaged.

3. An experiment to test the effect of an envelope made of polyethyleneterephthalate film on wood hygroscopicity.

3 x 3 x 3 cm. cubes of deal wood were made. All of them had a constant moisture content of 12%. Then, they were weighed and placed inside a dessicator with a 100% relative humidity. A week later they were weighed and the absorbed moisture quantity measured.

Tests involving cubes packed in an envelope had an absolutely identical procedure. According to the data obtained it may be indicated that moisture absorption of open cubic samples equals 13.4% while that of isolated ones is 5.3%.

Drying tests to assess water yield were carried out and experimental data suggest that an envelope reduces moisture effects by one third.

A painting of the seventeenth century Spanish school - "Escorial" was enveloped in the All-Union Central Scientific Research Laboratory for Conservation and Restoration of Museum Artistic Works (WCNILKR) in 1972. It is painted on wood. In the process of restoration it was parquettted on a metal parquetage, and the rear side of the painting is observed thanks

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It is painted on wood. In the process of restoration it was parquetté on a metal parquétage, and the rear side of the painting is observed thanks to transparency of the envelope.

This picture was placed under the conditions of variable relative humidity changing from 40% to 80% and suffered temperature fluctuations exceeding 10-15°C. It is known that a 40% difference in relative humidity of ambient air causes irreversible structural changes in cellulose materials. Observations have so far noted no changes in the painting.

Technology of producing such an envelope is very simple. Its transparency makes it possible to watch the rear side of a painting both visually and with the help of measuring instruments. It is recommended to be applied for paintings made on paper, canvas and other materials.

At present, envelopment of paintings is not a subject of argument in museum practices. Based on numerous observations and research efforts undertaken, especially, in the seventies, conclusions were made about absolute expediency of envelopment making use of various materials to produce envelopes securing qualitative environmental protection of paintings.

Envelopment is acceptable for all museums.

78/12/2

THE TRANSPORTATION OF A CONSIGNMENT OF
PAINTINGS FROM CAPE TOWN TO SOUTHAMPTON
BY SEA, SEPTEMBER, 1977

Peter Cannon-Brookes

National Museum of Wales
Cardiff 1
U.K.

ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

THE TRANSPORTATION OF A CONSIGNMENT OF PAINTINGS FROM CAPE TOWN TO SOUTHAMPTON BY SEA, SEPTEMBER, 1977

Peter Cannon-Brookes

Abstract With the rapid growth of air freight operations the advantages of transporting works of art by sea are often neglected. A consignment of seventeen paintings was transported in September 1977 from Cape Town to Southampton on board R.M.S. Windsor Castle and apart from the not inconsiderable financial economies achieved the increased wear and tear to which these paintings were exposed, unavoidably on account of vibration and changes in relative humidity, were reduced to a level virtually unattainable in transportation by air.

During the post-war years the enormous expansion of air travel has led to an equally rapid decline in the number of ocean liners operating scheduled services and there has been a tendency to transport works of art by air automatically without serious consideration being given to alternative transportation strategies. The author was confronted early in 1977 with the problem of transporting a consignment of seventeen Old Master paintings from Cape Town to Birmingham, England, and the two largest paintings in simple packing cases measured over 4m. by 2½m. If packed in these light-weight cases alone it was impossible for them to travel upright in the air freighters then operating out of Cape Town, and the cost of diverting a larger air freighter from Johannesburg and trans-shipping in Europe was excessive. Furthermore for air transport these paintings would have had to be double-cased for safety, adding still further to the problems of handling and to the cost. At this juncture contact was established with the Union Castle Line and the mail rooms of R.M.S. Windsor Castle were surveyed whilst she was in dock in Southampton in early May 1977.

Firm assurances were received from the Chief Engineer that the relative humidity in the forward mail room, which had a slightly wider doorway than the rear mail room and greater head room, was normally maintained at 60-65% throughout any voyage and that the low frequency engine vibrations were virtually negligible that far forward in the ship. A transportation strategy was evolved in which the cost of flying an escort (the author) out to South Africa and his travel back on board R.M.S. Windsor Castle was balanced against the reduced insurance premiums negotiable and the special freight charge quoted

by the Union Castle Line for carrying a high value consignment of cases of paintings in one of the mail rooms as passengers' luggage. To this was added the further economy of transporting the consignment in light-weight cases only, and the total estimated cost was well under one-half of the quotation received from the airline company for diverting a wide-bellied freighter to Cape Town, excluding the insurance premium payable and the cost of double-packing. It should also be noted that refined packing techniques, like the materials required for them, are unfamiliar in South Africa, and few contractors are able to carry out double-packing to the standards increasingly demanded in North America and Western Europe. On the basis of the quotations received, and in full awareness of the local difficulties likely to be experienced if air transport was to be attempted for the larger items, the decision was taken to transport the whole consignment by sea in the forward mail room of R.M.S. Windsor Castle, packed in light-weight cases only but with plenty of dunnage.

During packing in Cape Town sensors were installed inside one larger case and one smaller, and after stowing the consignment securely the cables leading from these sensors were linked to a Grant Miniature Temperature and Relative Humidity Recorder, Model 'D', set to record at hourly intervals so as to provide a continuous record of the temperature and relative humidity in those two sample cases at regular intervals throughout the voyage. Twice daily spot checks were made in the forward mail room using a standard whirling hygrometer, which proved to be of vital importance when the accumulators supplying the recorder failed in the middle of the voyage. Meanwhile records of the ambient temperature and relative humidity were made three times daily by the ship's officers and the results are plotted on the graphs below.

During the voyage the ambient temperature varied from 13°C to 28.8°C and the ambient relative humidity from 63% to 100%, whilst within the mail room the range of temperature was slightly reduced to between 16°C and 30°C with the relative humidity, after the first hours of the voyage, limited to the range of 61% - 68%. The discrepancy between the maximum ambient air temperature outside the ship and the maximum recorded within the forward mail room was due to the conduction of heat through the steel structure of the vessel whilst in the tropics and the close proximity of the hatch covers to the doorway. Unfortunately the progressive failure of the recorder and the eccentricity of many of the readings obtained make the individual measurements unreliable, but the trends are clearly identifiable in that the conditions within the larger case took some 12 hours longer than those in the smaller case to adjust to the mean conditions of temperature experienced within the mail

room and after 36 hours both cases were apparently conforming closely to the mean. Since the temperature changes before the last two days of the voyage were relatively gradual, with fluctuations over a comparatively small range, the changes in relative humidity within the wooden packing cases provided with plenty of dunnage can, after the first 36 hours, be safely assumed to have been close to the 61-68% range of the air within the mail room or even less.

In theory it would have been preferable to have made the spot checks earlier in the morning and in the early afternoon, at the extremes of the daily cycle, but security considerations, including the close proximity of the bullion locker, made this difficult. Furthermore there is evidence that without the opening of the mail room twice daily an even greater stability of relative humidity within it might have been achieved, with the avoidance of any possible inflow of hot air from under the hatches, and a remotely operated hygrometer viewed through a glazed inspection panel would have been an advantage.

The R.M.S. Windsor Castle is fully stabilised and in common with most modern ships on the mail routes her mail rooms were ventilated from the main air conditioning ducts without any outlet ducting. Thus a positive pressure system was operating and any natural leakage was outwards only. The mail rooms, unlike all other areas of the ship, were not equipped with automatic water sprinklers - an important consideration if an emergency or an equipment failure was to occur - though like the holds the mail rooms were equipped with a Carbon Dioxide fire smothering system. Access for the larger cases was only possible through the main hatches and in the event all the cases were swung on board using new slings, in pairs, and were unloaded using the same precautions.

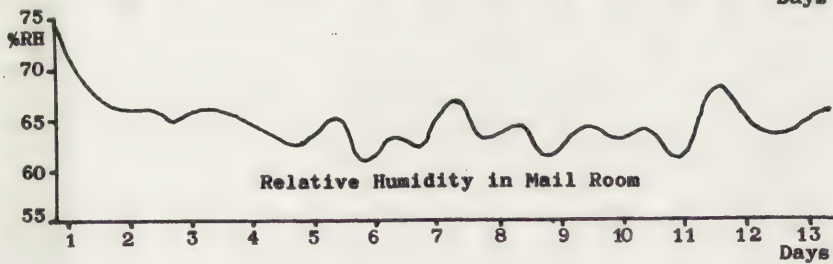
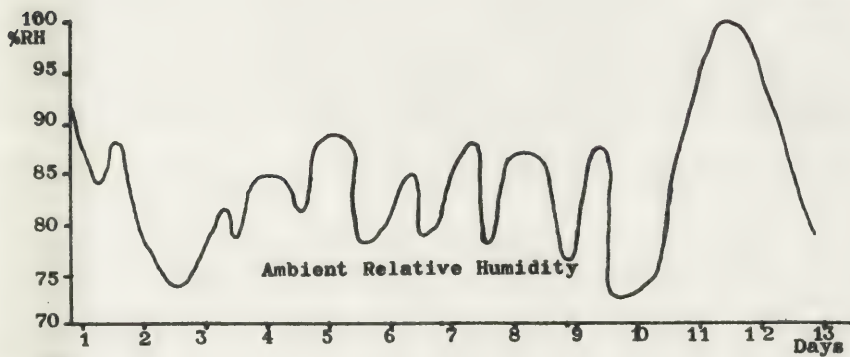
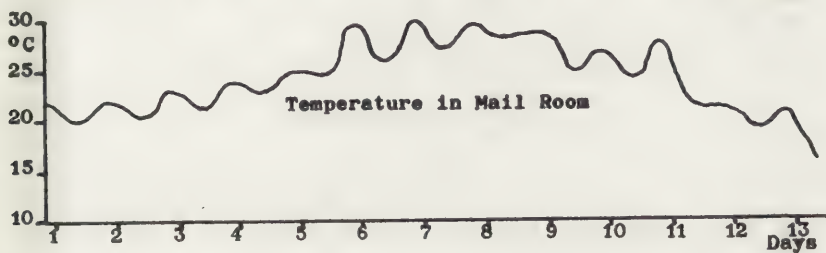
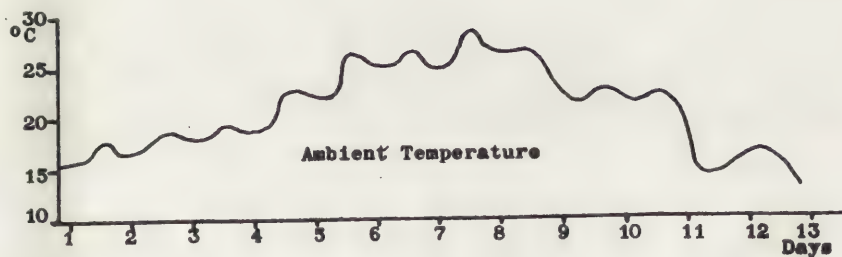
Between the National Gallery of South Africa and the Cape Town docks, a distance of less than three kilometers, the cases were transported in a standard van driven very slowly, but between Southampton docks and the City Museums and Art Gallery of Birmingham additional cushioning material was provided around the cases to compensate for the light packing within them. After unpacking in Birmingham the condition of the paintings was, on the basis of close visual examination, unchanged from Cape Town, and, whilst very considerable economies had been achieved over the quoted cost of transport by air, the increased wear and tear to which the paintings had been exposed, unavoidably due to the vibration and changes in relative humidity during transportation, had been reduced to a level virtually unattainable in transportation by air. R.M.S. Windsor Castle is now a floating

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hotel and mail ships no longer sail regularly between Southampton and South Africa, but in the evolution of any transportation strategy for other routes the advantages and economies to be gained from transportation by sea are worthy of careful consideration despite the longer time required.

Note: I wish to express my thanks to Stephen Rees-Jones, Keeper of the Department of Conservation, City Museums and Art Gallery of Birmingham, for his assistance in setting up the recording system and in the analysis of the results.

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78/12/3

THE PACKING OF CULTURAL OBJECTS:
THREE MEXICAN EXPERIENCES

Alejandro Rojas Garcia

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

THE PACKING OF CULTURAL OBJECTS:

THREE MEXICAN EXPERIENCES

Alejandro Rojas Garcia

Abstract

The author describes three case histories relating to recently developed techniques in Mexico for packing and transporting works of great cultural importance. The first refers to improvements in packing cases where the reinforcements are more effectively designed. Here, polyurethane foam is used as a cushioning material. The second experience describes a specially designed polyester glass fiber case reinforced with steel members used for safely transporting very precious ecclesiastical robes to Chicago. A system of interlocking trays with polyurethane fittings was employed. The final case history is the transport of a massive Olmec head to Spain by air freight in which the author describes the support and handling systems.

1. In conventional packing cases of wooden construction we have changed the traditional method of re-inforcement (re-inforcing members parallel to edges) to a diagonal system using x-members on each face. The wood we use is that of Ceiba, which is a non-resinous species, commercially available as boards or in plywood form of different thicknesses. This wood also readily takes lacquer coatings for surface protection. The method of closing of the lid of the case is by means of a nut-and-bolts system in which the nuts are recessed firmly in position into the wood structure, and the bolts are subsequently screwed down by means of a ratchet wrench. These fasteners are designed for flush mounting.

As regards cushioning materials, we use polyurethane foam which generally surrounds the object in mould-like fashion. A special saw is used to form or cut out the polyurethane so that an exact space can be formed to fit around the object. The foam material is in two sections - upper and lower ones.

2. The second experience concerned the transportation of a collection of works of art in textiles. Here the wood case was substituted by a construction made of fibreglass and polyester resin. This system is lighter in weight, more resistant and waterproof, and flame retardant to a degree. It is more expensive, however; three times more so than conventional wood construction. This project was possible according to rigorous conditions specified (for the first time) by the National Vice-Regal Museum (Virreinato, Tepotzotlan) for the loan to the Art Institute of Chicago of an important collection of Mexican textile objects from the treasure of the Mexico Cathedral. The object of greatest value to be sent was a Dalmatic garment of the 18th Century. The Art Institute of Chicago underwrote the cost of the unique packing system.

The fibreglass and polyester construction was internally re-inforced with an internal iron framework. This enabled recessed handles to be installed for carrying purposes. In the interior of the case there was provision for 5 shallow stacking trays, 15 cm. height, which individually contained the textile works of art. The individual objects were packed around polyurethane forms and moulds using wool flannel as a pre-wrapping and isolating material. The closure devices for the case were of the pressure type so that the lid could be hermetically sealed. Finally, the case was finished in an orange colour so as to be readily distinguished at customs and at airports.

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3. The third experience concerns a very heavy and large Olmec head. We noted that a cargo plane can only take a load of 3 tonnes (metric) per pallet. To transport the Olmec head (V) it would be necessary to spread its weight of $3\frac{1}{2}$ tonnes over two pallets. To meet this requirement the following system was devised which could take a supporting structure of $2\frac{1}{2}$ tonnes additionally. As illustrated, the Olmec head lying horizontally is placed over a bed of polyurethane foam which is placed over two structural steel support surfaces. Underneath these are five rectangular section steel supports which have an understructure of diagonally arranged steel tie-rods. This understructure rests on thick panels of plywood which distribute the overall weight (Olmec head and supporting structure) over a large surface area. Additionally a metal framework was installed overall for placing a protective tarpaulin against inclement weather.

In this manner the Olmec head was transported to Spain in 1977.

78/12/3/4

Fig. 1

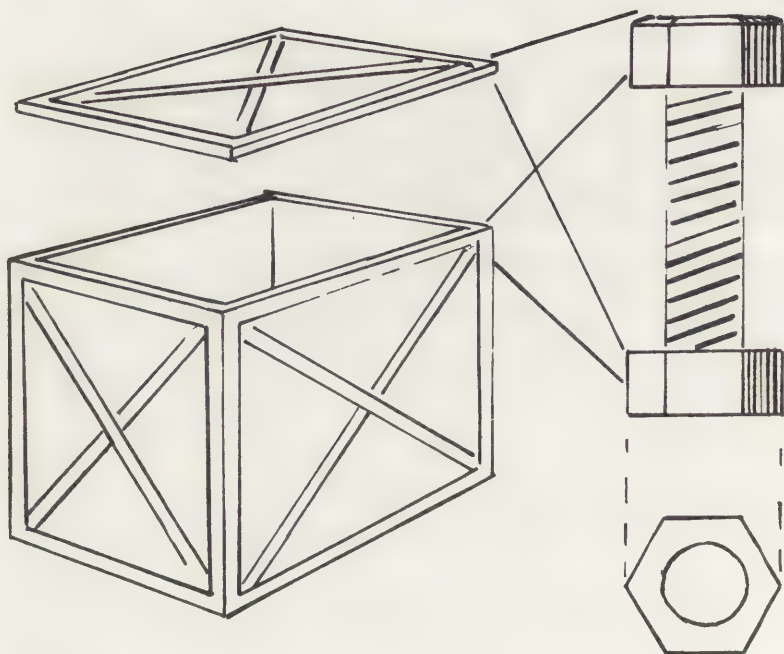
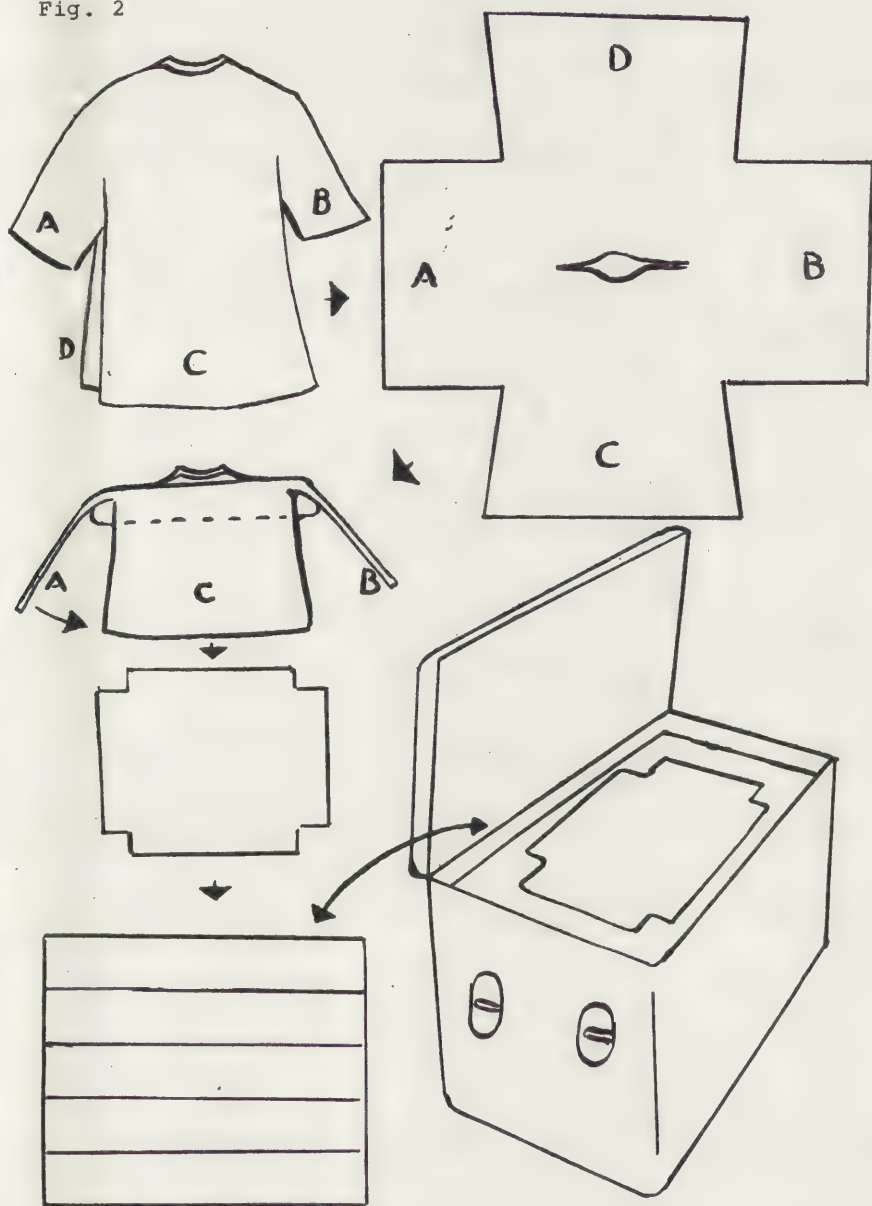


Fig. 2



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Fig. 3



COLLECTIONS D'HISTOIRE NATURELLE

Coordinator : G. Meurgues (France)
 Assistant coordinator:
 Members : Bacescu (Rumania)
 Barry (Rep. of South Africa)
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 responsables conservation Natur-
 historisk M. Universitetet,
 Arhus (Denmark)
 responsables conservation Northern
 Arizona Society of Science and
 Art, Flagstaff, Arizona (U.S.A.)
 responsables conservation Carnegie
 Museum, Pittsburgh, Penn. (U.S.A.)

Programme 1975-1978

1. Sujets Botanique:

Mise au point d'une technique de préparation, de présentation et de conservation de végétaux (Cryptogames et Phanérogames) destinés à des galeries de Botanique par application de la technique de lyophilisation ou de toute autre technique permettant la conservation des formes et des couleurs.

Mise au point d'une technique de préparation de modèles végétaux destinés à la constitution de dioramas.

2. Sujets Zoologie:

Conservation des peaux destinées à la naturalisation des Mammifères. Amélioration des techniques de tannage utilisés dans les musées.

Mise au point d'une technique de préparation et de conservation des Poissons.

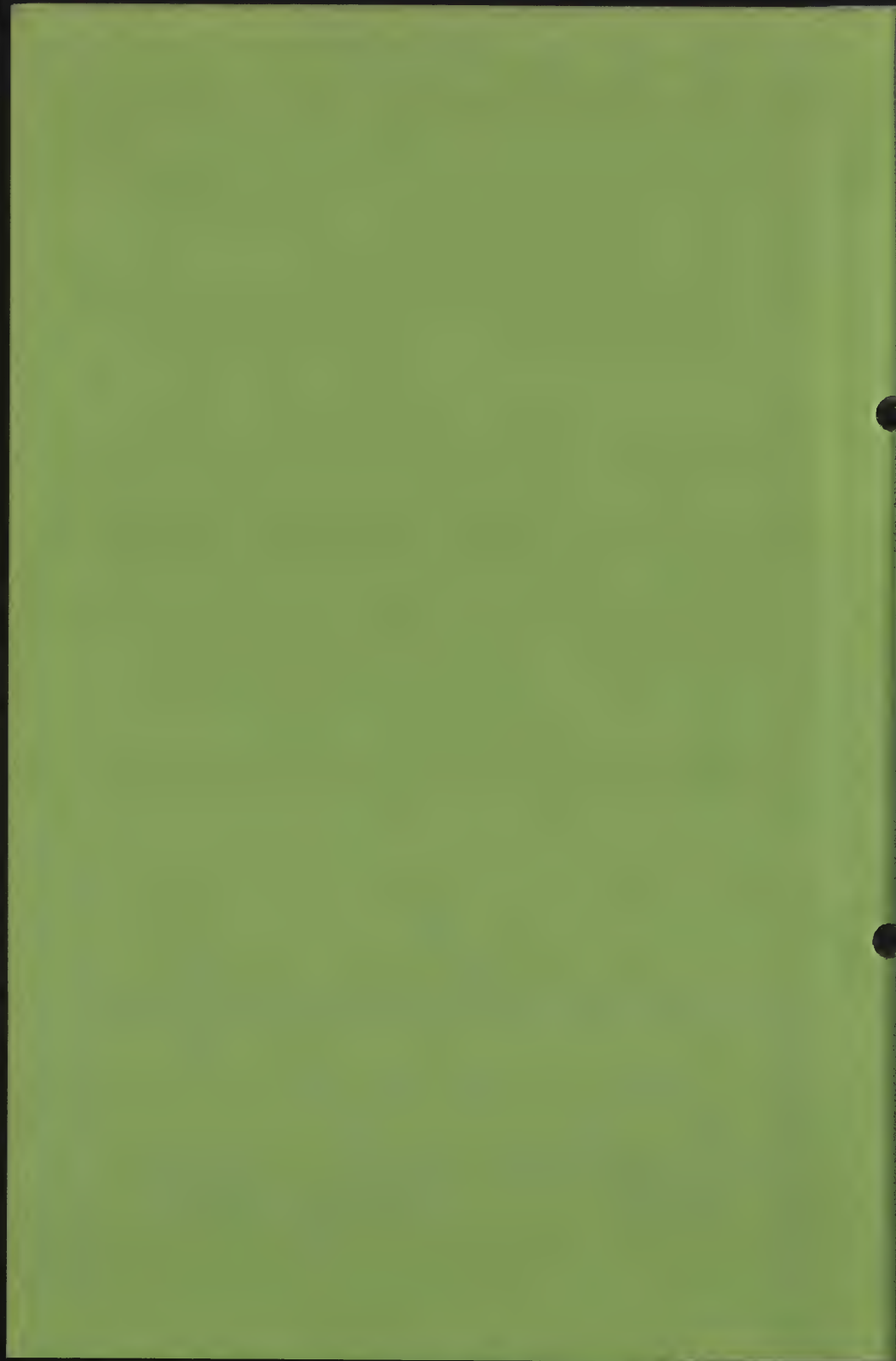
Préparation et conservation de Mollusques naturalisés.

DERMESTIDAE BEETLES INJURIOUS TO MUSEUM
OBJECTS AND PROTECTION MEASURES AGAINST
THEM

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5th Triennial Meeting
Zagreb, 1978



DERMESTIDAE BEETLES INJURIOUS TO MUSEUM OBJECTS AND
PROTECTION MEASURES AGAINST THEMG.A. Zaitseva

Beetles of Coleoptera order, Dermestidae family, belong to one of the most important groups of insects destroying keratin-containing materials in the USSR museums. Dermestidae family is comparatively small in number. According to R.D.Zhantiev, 135 varieties of Dermestidae have been recorded in the USSR. Although the proportion of injurious varieties among them is overwhelming. It amounts to one third of the entire number of Dermestidae varieties in the USSR fauna, i.e. 42 varieties. About 20 Dermestidae varieties are recorded in museums of this country.

The life cycle of the predominant number of Dermestidae varieties (egg-larvae of p-stages-pupa-imago) successfully passes at 10 to 42°C and 80% relative humidity maximum. Optimum temperatures and relative humidity rates correspond to 20-30°C and 35-50% accordingly, that is being within the range allowing to regard Dermestidae beetles as insects preferring warmth and aridity. In the Southern parts of the USSR noted for temperate air humidity the varieties of Dermestidae beetles as well as the quantity of species are greater in number. Thus, their incidence in Central Asia is greater than in the Central area of the European part of the Soviet Union. Natural sources of Dermestidae beetles are nests of birds and burrows of animals. The initial food substrata of Dermestidae larvae in these biotopes: fur, feathers, skin, bones, etc. determine a wide spectrum of museum materials damaged by larvae

including those worked up to a certain extent just as well.

Dermestidae beetles can invade premises and, in particularly, museums directly from natural environment. This encroachment is facilitated both by adequate temperature and humidity levels and an abundant choice of food substrata. The parameters indicated, evidently, determine sinanthropisation of Dermestidae beyond sharp dependence on geographical latitudes. It can be exemplified by recording a steady population of motley beetles - Anthrenus picturatus Sols in one of the museums functioning in the Vologda Region (North-West of the USSR) though these insects are mass destroyers of various products and materials in the South of the country. Dermestidae varieties whose imagos (beetles proper) do not require absolutely necessary additional nutriment of nectar and flower pollen or do not have to eat at all to lay eggs, have a greater tendency to spreading in museums. Thus, Attagenus smirnovi Zhant, initially recorded at the beginning of the sixties became a dangerous insect in Moscow museums in a short span of time. To lay ample eggs these beetles do not require additional nutriment. Attagenus smirnovi makes it worse by fast development; its life cycle is completed in three months.

Adult beetles perform functions of reproduction and settling about, the latter being pursued actively by impregnated females flying out in search of adequate substratum to lay eggs in and, at the same time, to feed larvae. It is Dermestidae larvae that actually damage museum objects. They intensively devour and grow accumulating fats, carbo-hydrates required for complex and energy-consuming transformations of larvae into pupae and, finally, imagos. While growing, larvae moult

with new coverings forming and the old cuticle casting. The number of moults can vary from 5 to 10-12 and even more. The increased number of moults indicates unfavourable conditions for larvae. Trogoderma variabile Ball. can serve as an example with its larva development being delayed up to five years due to an endless number of moults under unfavourable conditions.

Among the Dermetidae varieties occurring in the country's museums Anthrenus Schaeff and Attasenus Latr. are most injurious to museum objects. It is on their account that the spectrum of museum objects damaged by Dermetidae is extraordinary wide. It covers not only stuffed animals, skeletons, carcasses of birds and animals, exhibits made of fur, feathers, horns, skins but also all sorts of domestic and aesthetic objects made of wool, silk or incorporating fragments of these materials. Species of Dermestes L. genus from which the name of the family proper originates occur less frequently in museums. Animal hides, skins of stuffed animals and bird carcasses are favourites of this genus's larvae to feed on, incompletely dried substrata being the most preferable for larvae of Dermestes genus. Grubs of moths (Lepidoptera order, Tineidae family) and Dermetidae larvae damage a nearly identical choice of keratin-containing materials in museums. Traces of activity of these two important groups of pests should be distinguished which is essential for a successful choice and preventive and insecticidal treatment at a later stage. Bores made in some substratum by grubs of moths and Dermetidae larvae are difficult to discern. However, injuries caused by grubs can be identified by excrements and web texture soiling the material as well as grub and pupa covers cast. Only bores are actually left behind. Excrements of Dermetidae larvae

are fine and dust-like and are as easily shaken off the material as moults cast by larvae. Therefore, in case of even an insignificant replacement of an exhibit we record only "clean" bores which does not suggest in any way remoteness of damage in terms of time.

Efforts are underway in the All-Union Central Scientific and Research Laboratory for Conservation and Restoration of Museum Artistic Works to elaborate preventive measures directed at protection of museum objects against Dermetidae. The study of organs of sense in Dermetidae larvae and imagos was one of the first stages of this work. Ascertaining the degree of development in Dermetidae's organs of sense and their localisation would give a chance of considering possibilities of these insects' perception of olfactory and gustatory stimuli.

An electron scanning microscope was used to examine beetles and grubs of various stages in the development of Dermetidae varieties - Anthrenus picturatus Sols, Anthrenus scrophulariae L. and Attagenus smirnovi Zhant. Each species was examined to include the surface of its head capsule, orifice appendages and horns or antennae. Sensiles of various types are concentrated on the antennae and palps (labial and maxillary) of Dermetidae larvae and imagos.

A sensile is an elementary faculty by which chemical, mechanical, sound and other irritations are perceived. In the simplest case it consists of three cells: a sensitive neuron perceiving and conveying impulses to the central nervous system, a nidus-building cell and a trichogenic cell to form the surface or cuticle section of a sensile. The form and position of a hair or its derivative determine the type of a sensile. There are trichoid (hairs proper), basiconic (short hairs or

cones with a rounded end), styloconic (cones with a papilliform end), placoid (cuticle section looking like a plate slightly overhanging the surface of cuticle) and many other sensiles.

Trichoid, basiconic and styloconic sensiles strongly prevail in imago and larvae of the above-mentioned Dermetidae varieties. Besides, a sensitive pore was detected on the antennae of Anthrenus larvae. As compared with larvae of many other species of coleopterous beetles (organs of sense were examined by Yu.A.Elizarov, 1975) diversity of sensiles in Dermetidae larvae is much less. Very similar "receptor zones" are at the end of maxillary and labial palps of Dermetidae imago and larvae. The palps are found directly at the astomatic orifice. Our term of "receptor zones" refers to spherical porous areas with styloconic and basiconic sensiles sticking out sporadically.

The position and types of sensiles on the larvae's antennae of two genera are different. Thus, the last antennary segment of Anthrenus picturatus and Anthrenus scrophulariae end up in larvae of all development stages with a large nephroid sensite. The last antennary segment of Attagenus smirnovi ends up with a "receptor zone" similar to palp ends but having one trichoid sensile.

Antennae of imago of all Dermetidae varieties examined are covered unevenly with sensiles. Their majority is concentrated on the last three enlarged segments - the mace. The antennae of male and female adults of Anthrenus are identical in form as well as in types and concentration of sensiles. Basiconic sensiles are scattered diffusely over the surface of the mace's segments and their joists. Female adults of Attagenus smirnovi differ from male adults by larger

sizes and a shorter last segment of their mace. The indicated genital dimorphism corresponds to sensiles' situs. The surface of the males' last antennary segment evenly covered with trichosensiles has a number of spherical recesses of the cuticle with basiconic sensiles in them which is not the case with females.

Styloconic and basiconic sensiles of imagos and larvae of Dermetidae are concentrated on the ends of maxillary and labial palps in "receptor zones". Such a distribution of sensiles in the above-mentioned varieties is similar to that of larvae of click beetles (Agriotes family), grain borers (Anisoplia austriaca) and grubs of butterflies. According to Yu.A.Elizarov (1977) these groups of sensiles of the above-mentioned insects act as contact chemoreceptors. In this it is appropriate to suppose the analogy of functions just as well, all the more the major purpose of contact chemoreceptors is to detect suitability of a substratum for eating and egg laying.

Olfactory sensiles of the majority of insects are based on antennae. Trichoid and basiconic sensiles found in great numbers on the surface of Dermetidae imago's last antennary segments function as typically olfactory receptors.

The information obtained indicates a more developed system to perceive various stimuli possessed by Dermetidae imagos. Originality of organs of sense on the larvae's antennae determines differentiation of further working methods aimed in the long run at decoding larvae's search for food substratum.

While attraction of natural food digested by Dermetidae larvae: fur, feathers, skin, etc. is beyond doubt an appropriate experiment was required to define the degree of attraction of various museum tissues and

cloths. Larvae of three Dermetidae varieties: Altagenus smirnovi, Anthrenus serophulariae, Trogoderma variabile Ball, were offered a choice seven types of most widespread museum cloths to feed on. It included (1) home-spun wool dyed in natural dyestuff; (2) thin wool fabric dyed in aniline; (3) cloth made of pure silk (natural dye); (4) Central-Asian silk made from silk fibres and a weft of cotton threads (aniline dye); (5) classic velvet with silk pile and cotton lining; (6) cotton cloth; (7) linen.

Larvae of the given Dermetidae varieties preferred wool fabric to all the rest of cloths. Dyes, apparently, did not play the decisive role in this choice for while Anthrenus serophulariae larvae ate up wool in large quantities Altagenus smirnovi larvae more willingly devoured thin wool fabric. Cloth of pure silk was also accepted as food by larvae though to a lesser extent. Central-Asian silk and classic velvet made of threads of two types were attacked selectively by Dermetidae larvae. They destroyed silk fibres leaving cotton ones intact. "Pure" cotton cloth, however, turned out to be attacked though very insignificantly. Cloth made of flax demonstrated the highest pest resistance.

Wool fabric, therefore, can be employed as a positive test in experiments with Dermetidae larvae. Comparison would make it possible to assess both attractive and repellent properties of the substance under investigation.

A package of measures is required to provide reliable protection of museum objects against Dermetidae beetles - dangerous pests well-adapted to museum conditions. Preventive treatment of museums against Dermetidae infestations should be based on Knowledge gai-

ned in biology of Dermetidae varieties damaging to museums with due regard to museum peculiarities. Preventive measures of this Kind for historical, art-ethnographic, local lore and other museums should be worked out proceeding from these too principles:

- absolute harmlessness of measures proposed (in particular, in application of agents to be used as repellents and attractants) for museum personnel and visitors;
- absence of unfavourable effects of recommended conditions, agents, etc. on museum objects.

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WOOD PESTS IN ARTICLES AND STRUCTURES
AND PEST CONTROL IN MUSEUMS

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Zagreb, 1978

the first of these is the fact that the
 system is not self-sufficient. It
 requires a constant supply of
 raw materials and energy. The
 second is that the system is not
 self-correcting. It requires
 constant human intervention to
 keep it running.

The third is that the system is not
 self-sustaining. It requires a
 constant supply of capital and
 labor. The fourth is that the
 system is not self-renewing. It
 requires a constant supply of
 new technology and innovation.

The fifth is that the system is not
 self-organizing. It requires a
 constant supply of human
 organization and management.

The sixth is that the system is not
 self-regulating. It requires a
 constant supply of human
 regulation and control.

The seventh is that the system is not
 self-optimizing. It requires a
 constant supply of human
 optimization and improvement.

The eighth is that the system is not
 self-adapting. It requires a
 constant supply of human
 adaptation and change.

The ninth is that the system is not
 self-evolving. It requires a
 constant supply of human
 evolution and progress.

WOOD PESTS IN ARTICLES AND STRUCTURES AND PEST CONTROL IN MUSEUMS

I.N. Toskina

Entomological efforts by experts in entomology in the USSR museums have been underway for over 15 years. About one hundred various museum repositories in different towns of the European part of the USSR excluding the Baltic Republics, Byelorussia, the Western Ukraine, Moldavia and Transcaucasus have been inspected in this period. We are of the opinion that harmful entomofauna of museums in the covered region could be regarded as ascertained in principle.

The field collected insect species could be subdivided conditionally into three groups by materials attacked: (1) wood-destroying pests; (2) insects attacking keratin-containing materials; (3) insects attacking starch-containing materials and paper.

In the European part of the USSR we encountered wood-destroying insects representing four families: Anobiidae (borers), Curculionidae (weevils) - subfamily of Cossoninae, Cerambycidae (capricorn beetle), Lyctidae (wood borers). Anobiidae beetles are considered to be of a greater importance as insects injurious to old wood. They damage and destroy the wooden base of paintings, collections of peasant houseware, wooden sculpture and furniture as well as structures. Biology of anobiidae is poorly studied and, therefore, it hinders verification of ways and means of control measures against these insects. Control of these beetles hitherto remains not only laborious but often scarcely reliable just as well. Insufficiency of studies in biology of anobiidae is due to the beetles'

peculiarities: (1) they are small in number in natural conditions which handicaps experimental specimen collection and natural observation; (2) their development even in one generation is extremely disproportional; (3) their grubs have a reserved way of life inside wood and those of the majority of varieties develop very slowly.

All in all, eleven varieties of Anobiidae (excluding Stegobium paniceum L. related to beetles injurious to materials of the third group) have been encountered as wood-attacking insects in the European part of the USSR. They are enumerated in Table 1. As it is illustrated by the Table A.punctatum is the most widespread species. It is recorded both in the North and in the South but in the Central and Northern areas it inhabits heated dwelling. This "cosmopolitan" was carried in infested furniture to all the continents, except Antarctic. Its birthplace is likely to be N.-W. Europe with its mild winter and temperate summer.

The rest of Anobiidae varieties come to museums from the local fauna.

Pr. confusum, Pr. pertinax and, to a lesser extent, Pr. carpini are the major types of insects injurious to unheated structures in the Northern parts. The first type has never been outlined by West European literature as a wood-destroying insect at all while the second one has been mentioned far too rarely. Biology of these species, like biology of the majority of Anobiidae varieties, is very poorly studied. According to our laboratory observations the beetles of these three varieties usually become active after 6 o'clock in the evening. A few eggs are laid by female species in chinks and old holes in two or three dozens in average, one by one or in small heaps. The egg cover is

thorny to help it stick in the smooth slits. Embryonic period of Pr. pertinax lasted from 3 to 4 weeks while that of the other two varieties from 2 to 3 weeks under room temperature and at relative humidity of not less than 70 per cent. When the grubs are out, they devour some of their egg cover and start to look for the place to bore in wood. They have negative phototaxis, i.e. tend to avoid light. Due to the small size of grubs their inlets are practically invisible to the naked eye. Grubs of all the above species develop slowly - it takes several years before the larva that enters wood turns into a beetle that flies out. Pr. confusum settles only in softwood, Pr. pertinax prefers to do so while Pr. carpini is recorded both in softwood and hardwood but usually with traces of fungal diseases. All the three species require negative temperature in winter time, therefore, they are found in unheated structures and outside walls of dwelling-houses.

Table 1

Anobiidae injurious to wooden exhibits
of museums in the European part of the USSR

Anobiidae varieties	Anobium punctatum DeG	Priobium confusum Kr.	Pr. pertinax L.	Pr. carpini Hbst.	Cacotemmus rufipes F. (Anobium rufipes F.)	C. thomsoni Kr.	(A. thomsoni Kr.	Ptilinus fuscus Geoffr.	Oligomerus brunneus ol.	O. ptilinoides Woll.	Nicobium schneideri Rtt.	Ernobius mollis L.
Places (North to South and West to East) in which pests' incidence is recorded	1	2	3	4	5	6	7	8	9	10	11	12
Karelian ASSR (Petrozavodsk Dist.)		+	+	+								+

1	2	3	4	5	6	7	8	9	10	11	12
Leningrad	+										
Vologda District	+	+									+
Novgorod "-	+	+	+	+							
Yaroslavl "-	+	+	+								
Kostroma "-	+	+		+	+		+				
Kalinin "-	+										
Moscow "-	+	+	+	+	+	+	+				
Moscow	+	+			+						+
Vladimir District	+		+		+						
Gorky "-	+						+				
Smolensk "-	+				+						
Kaluga "-	+										
Tula "-	+			+							
Ryazan "-	+							+			
Mordvinian ASSR	+										
Bashkir ASSR	+										
Kiev	+								+		
Rostov District	+										
North-Ossetian ASSR	+										
Daghestan ASSR	+								+	+	+

Pr. carpini occurs in locations characterized by conditions most favourable for house fungi, i.e. with high humidity and poor ventilation. Pr. confusum prefers boundary areas with greater currents of air and, consequently, a lesser degree of humidity. House fungi in such areas develop slowly or cease to grow at all. This species is very susceptible to high summer temperatures and its incidence is recorded in our Central parts where it infests Northern walls of unheated structures. Pr. pertinax occupies cold sides of lower

parts of structures and settles in beam joints, i.e. poorly ventilated and, therefore, damp places. The Northern boundary of Pr. carpini's injuriousness does not coincide with that of its area. This species, evidently, does not sustain wintering in cold structures exposed to the wind and settles somewhere close to the ground.

One and the same object is often infested by two or even three varieties of Priobium. It is mostly recorded together with Pr. confusum and Pr. pertinax. It was not possible to define distinct boundaries of their areas but they are likely to overlap each other. When an object is infested by Pr. pertinax and Pr. carpini the latter occupies the major section.

These varieties of Anobiidae settle in the upper layers of beams. Pr. Confusum and Pr. pertinax were also encountered in thin slips of wood used in old fences, so wood thickness is not essential.

In Central parts of this country C. rufipes and, especially, Pt. fuscus are highly injurious. These varieties penetrate timber in cold structures the way the previously mentioned varieties of insects do. The former is a hydrophile to the utmost but has hardly anything to do with fungal attack occurring in wood. In structures it mostly damages the sills of beam joints. Indoors, where high humidity prevails, we encountered this variety of Anobiidae penetrating all sorts of objects from furniture to objects made of thin plaited roots. In large beams of 18-20 cm in diameter C. rufipes destroys mainly the upper part (one third) of timber (5-6 cm).

Pt. fuscus settles only in hardwood. It is, apparently, to a lesser extent a hydrophile as compared with the previous variety: its attack is not confined

to beam joints. Timber infestations of Pt. fuscus can be recognized by typical, very large heaps of bore meal that pours out of tunnels. Timber is injured to the core.

In Southern and South-Western parts of the country, apart from A. punctatum, considerable damage is caused by O. ptilinoides and N. schneideri. Varieties of Oligomerus are less susceptible to humidity but higher summer temperatures are required for their growth. The optimum temperature for the growth of O. ptilinoides is within the range of 20-32°C and no growth occurs when the temperature drops below +14°C (Parfentier, 1953). As compared with A. punctatum it infests warm and dry sections of structures and develops only in hardwood.

N. schneideri is referred to the most thermophile varieties in the area covered. Its incidence is recorded on the coast of the Crimean Peninsula, Transcaucasus, Western coast of the Caspian Sea, that is in the warmest East European parts, at the same time nearing the sea. N. schneideri mostly grows in softwood but also occurs in hardwood (Parfentier, 1952). Thickness of the wooden object affected by this variety is of no importance either: it penetrates plywood along with timber and planks.

The attack of other varieties of Anobiidae (C. thomsoni, O. brunneus, E. mollis) is less evident. Development of E. mollis is always connected with the presence of bark.

Development of nearly all the varieties takes not less than two years. In optimum conditions A. punctatum develops in two-four years, hence wood infestation is not spotted immediately and this contributes to spreading infested objects around. Omnivorousness of

A. punctatum is yet another reason for its wide spreading. It penetrates both hardwood and softwood, enjoys plywood, injures objects made of roots, develops in dry plaster, cardboard, even inside insetted book, but does not affect chip boards since their adhesive contains urea-formaldehyde resin.

Biology of A. punctatum is studied beter than that of other varieties but it is far from being completely covered. Eggs are laid by female species one by one or in small groups of about 20 on face planes, as if "inserted" between wood fibres, into holes, roughness, chinks, etc. Eggs are not laid on smooth, especially polished surfaces. Young grubs cannot bore in wood through such a surface without having anything to steady against. Therefore, a thorough treatment of surfaces, primarily butting ends, with spreading varnishes and oil paint over them and plank joints could serve as preventive measures to protect wooden objects.

According to our observations 14-16°C and a 15-18% moisture content of wood corresponding to 70-80% relative air humidity are optimum conditions for embryonic development of larvae. At a later stage, an 18-20% moisture content of wood is optimum for their development as it was recorded by Persov (1970).

A. punctatum does not stand high temperatures: at 30°C adult females sink into a thermal torpor and in a few days of such heat become incapable of laying eggs, embryonic development continues in the egg but larvae can hardly emerge and fail to bore in wood. At 34°C the embryo is destroyed. The following extreme conditions are also recorded in literature: air humidity of 45 per cent is critical at the moment of producing larvae (Spiller, 1948), that is Anobiidae dies out in

dry premises; 80-100 per cent of larvae are destroyed at a sudden drop of temperature to 16-17°C in 48 hours (Parfentiev, 1947). Larvae are especially liable to be affected by frosts during their first year of development.

We went on with tests initiated by Parfentiev to destroy A. punctatum by cold. Four heavily infested panels of icons 3-4 cm thick were carried out to cold premises in autumn where they were kept till next spring. The temperature there averaged minus 5-10°C during three winter months. In mid-January it dropped to minus 18-20°C and did not change for three days to follow while at the beginning of February it stayed at minus 25-30°C for five days running. In spring the surface of the panels was thoroughly waxed, face planes, rough sections and holes were filled with melted wax. After that the icons were brought back to normal conditions to be observed for three years. During this period not a single fresh outlet hole appeared on their surface while beetles continued to fly out from the control panels. We believe that A. punctatum was destroyed by hard frosts in January and February while wax coating preserved wood from another infestation. During these years the wax coating was renewed several times for it adhered badly to heavily injured parts covered with borings.

To destroy Anobiidae in structures we carried out insecticidal tests. Insecticides were selected with long duration of efficiency and good solubility in ordinary solvents. Six sections of several square metres each were chosen in four dwellings heavily infested by Pt. fuscus. The following pesticide solutions were tested on every one of the six sections: 5 per cent DDT Cryst. in xylene, 5 per cent and 10

per cent DDT, 1 per cent lindane, 5 per cent and 10 per cent sevin, 10 per cent SPCPh (sodium pentachlorophenoxide) - all in acetone. DDT solutions were considered to be standard. Untreated sections as well as sections treated with acetone and xylene were control parts. Treatment was undertaken before beetles started to fly out. Saturation was performed once with a syringe to fill wood completely. The treated sections were observed for six years to follow marking new outlets.

Good results were obtained only with 10% pesticide solutions. A 10% solution of SPCPh in acetone proved to be most reliable. A technical compound containing 92% of pura substance was used in the tests. Solution consumption averaged 0.85 litre per square metre of surface. A 5% solution of SPCPh was not tested being unreliable since some of it is washed away with water and only 50% or so effected by vapours and CO_2 contained in the air is transferred to insoluble pentachlorophenol to remain in wood for a long time (Kalininsh, 1958).

SPCPh solutions have an effect on some painting materials (Kuritsina, 1968) and this compound is poisonous to warm-blooded animals. Therefore, it can be used for treatment of uninhabited structures only and only when there are no paintings inside.

Sevin caused a steady brown colouring of wood on external parts of walls, i.e. under the influence of weather factors.

x x x

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DOCUMENTS GRAPHIQUES ET ENLUMINURES

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Programme 1975-1978

1. La conservation, la restauration et l'analyse des cuirs et des parchemins utilisés en reliure (Chahine, Gallo, Schaffer, Zappala).
2. La restauration et la conservation des papiers, dessins, enluminures et manuscrits sur feuilles de palmier et écorce de bouleau (Agrawal, Hofenk-de Graaff, Kostikova, Nyuksha, Radosavljevic).
3. Analyse des encres et des enluminures par la chromatographie en phase vapeur et la chromatographie liquide haute performance (Flieder, Roelofs).
4. Etude de la microflore se développant sur les bandes magnétiques et les films (Kowalik).



THE CONSERVATION OF A 17TH CENTURY
OUTSIZED MAP

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5th Triennial Meeting
Zagreb, 1978



THE CONSERVATION OF A 17TH CENTURY OUTSIZED MAP

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Abstract: An outstanding masterpiece of cartography is the map of the canton of Zürich by Hans Conrad Gyger (1599 - 1674) which he completed in 1667 after 38 years of preparation. This work of art, unique in size, beauty and accuracy, is the first map of its scale based on trigonometric survey and the very first topographical map drawn in relief. It measures 220 x 230 cm and represents an area 70 x 75 km. It is made of paper and the design executed in an aqueous medium. In 1976 the map was brought to the Swiss Institute for Art Research for examination and conservation treatment. The technique of the map's fabrication, its damages and its treatment are described in detail. The map was backed with Japanese paper and thereafter lined with canvas. The uniqueness of this object, as well as its large size, made its treatment a task requiring the utmost care.

One of the greatest masterworks in the history of cartography is the map of the canton of Zürich produced by the Swiss cartographer Hans Conrad Gyger (1599 - 1674). Gyger completed the painted map after 38 years of preparation in 1667, and presented it to the government of Zürich one year later.

The map belongs without doubt to the most remarkable of achievements in the art of map-making. Unique in its size, accuracy and beauty, it is the first map of an entire Swiss canton based on trigonometric survey and the very first map drawn in relief. Modern cartographers describe Gyger's map as the most accurate topographical map of a region this size to be produced in the seventeenth century. The painting, which measures 220 x 230 cm and represents an area 70 x 75 km, has an effect similar to that of an aerial photograph, since mountains, hills and individual houses are portrayed in light and shadow with natural colors.

The richness of detail of this map is of inestimable value to geographers as well as historians. Bodies of water down to the smallest stream are shown, as are topographical pictures of cities, villages, barns, castles, cloisters, ruins, leper colonies, mills, inns, watchtowers, gallows, roads, bridges and ferries. If Gyger's map is compared with modern maps, changes in river courses, woodlands, croplands and vineyards can be easily ascertained as well

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as changes in cloisters and other sites. The map's accuracy was not surpassed until the cantonal surveys of 1850.

Today the map belongs to the State Archive of Zürich and hangs in the Rechberg House in Zürich as a permanent loan.

Condition before Treatment

At the time of the renovation of the Rechberg House the map had to be evacuated, and the opportunity was taken to have its condition examined by the Swiss Institute for Art Research. Various damages were found, which constituted a serious threat to the preservation of the artifact.

The examination provided the following picture of Gyger's working procedure: The topographical details were first sketched on individual sheets of paper with pen and ink. These sheets, none of which was larger than 51 x 77 cm, were numbered on the reverse and assembled on a canvas. The paper was adhered to the canvas with rye flour paste. The map consists therefore of 28 paper sheets of varying size and 10 narrow edge stripes, the supporting canvas of 6 pieces sewn together. The painting itself was executed in a lean, opaque distemper medium (analysed as animal glue) and remained unvarnished originally. There are also the four points of the compass at the map edges, a scale in the center, and a legend in the lower left which were written in ink on unpainted paper and subsequently pasted onto the picture. These were all, however, undoubtedly original, since they bear Gyger's handwriting.

Since such a precise map would have been valuable to a potential military enemy, it was at first withheld from public view and stored in the city hall. In the following centuries it arrived in various official buildings in Zürich, furnished with heavy round rollers. It was stored variously in a cabinet built just for the purpose as well as in dust and gloom. Since the 1830's the painting has been covered by a varnish, which is supposed to have suffered seriously during an exhibition in 1891. A painting firm received the commission to restore the map in 1919. This treatment, according to the firm's invoice which is still in existence, consisted of: Reinforcing the edges with cloth, cleaning, fresh varnishing and repainting of abraded inscriptions and coats of arms. The transformation of the rollable suspension into a rigid mounting on a wooden frame must also have taken place at the beginning of the 20th century. Through its attachment with nails the edges of the map were extensively punctured.

Much graver damages however were the characteristic compressed wrinkles and the tears in the paper which resulted from its being repeatedly rolled. Varnish penetrated

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through the tears to the canvas, which became extremely brittle and torn in places as a result of the oxidation of the absorbed varnish. This was the case to an extreme degree along the join of a long narrow piece attached to the upper edge of the picture. Although a few attempts had been made to reinforce the fabric here with patches at the reverse, the canvas threatened to tear clean through by the force of its own weight. The yellowed and extremely glossy natural resin varnish also penetrated into the paint layer and paper and radically changed their color. Unfortunately a few areas of the painting had been badly skinned during an earlier cleaning, sometimes leaving only the preliminary sketch visible. Several place names and inscriptions had also been washed away, indicating that someone must have once tried to clean the map aqueously. Those obliterated parts of the landscape were coarsely and carelessly repainted.

The paper had separated from the canvas at many of the tears and threatened to fall away. That no real losses larger than 1 cm² are to be reported is probably thanks to the circumstance that the picture had been stored behind glass for the previous 25 years.

Treatment

The map was brought to the Swiss Institute for Art Research in 1976, where it was examined and conserved in the Department of Restoration and Technology.

The mounting of a modern homogeneous piece of paper of this size presents difficulties already; the handling of an unevenly painted paper surface composed of 28 pieces and over 300 years old would be expected to be that much more difficult. The uniqueness of the object as well as its large size made its treatment a task requiring the utmost care. Therefore only those methods and materials were used which guaranteed as much reversibility as possible.

Since the old canvas no longer served its function as a support it had to be removed from the reverse. Therefore as a temporary support a facing of an English wet-strength tissue paper was applied with methyl cellulose adhesive to the face of the painting, which was still protected by varnish. The map was then attached face down by means of the facing to a specially constructed table, so that the canvas could be removed dry and in strips.

Flour paste residues were removed from the reverse of the paper mechanically, and the tears were mended with long fibre "Ino-Shi" Japanese paper and rice starch paste. The losses to the paper and the map edges, which were severely

damaged by nails, were filled with 17th century paper which was as strong as the original paper.

Strong, hand-made "Nisumi" paper was prepared for backing. 15 rectangular sheets (each 60 x 90 cm) were cut and their edges frayed with the aid of moisture. After rice starch paste was brushed on the sheets, they were placed individually on the previously moistened reverse of the map and then rolled on with a rubber roller. By means of careful placement and overlapping of the frayed edges (this paper is made of mulberry- and flax-fibres as long as 20 mm), practically seamless joints could be achieved. The backing was attached to the edge of the table with tape and allowed to dry slowly, without pressing.

As the actual support a 3 meter wide, seamless canvas was chosen. It was washed, stretched on a stretcher and ironed. In order to make it somewhat more resistant to environmental influence it was impregnated with Plexisol P 550 (an elastic butylmethacrylate), thinned with white spirit. Rice starch paste with 20% Mowiol 20-98 (a polyvinyl-alcohol soluble in water) added in order to increase its adhesive strength, was used as the "lining" adhesive. This paste was applied to the lining canvas which, still on its stretcher, was afterwards placed on the freshly moistened map reverse and rolled in place. The map, which had shown a severely distorted surface, drew itself completely flat as it became taut in drying.

After attachment to a new stretcher with brass tacks, the facing paper was slightly moistened with a sponge and could then be pulled off without any problem. The varnish was removed with a 1:1 mixture of ethyl alcohol and methylene chloride (and once again it could be seen how easily and gently such natural resin varnishes are removed). The old retouches could also be removed with the same solvents.

In order not to impair the documentary value of the object, the abraded areas and effaced inscriptions were not at all retouched. In fact, no retouching was carried out beyond the toning of the paper inlays with water colors. As a protective coating various resins in different concentrations were tried out, including Paraloid B-72, Calaton, Keton-N, Elvacites 2008 and 2044. Every one of these resins either altered the matt appearance of the colors or was absorbed by the paint and was only removable with difficulty. Therefore it was decided to forego a protective coating, especially since the map was to be housed in a fireproof plate glass case.

In addition to the restoration team of the Institute the following people contributed to the success of this project: Dr.B.Mühlethaler, Dr.J.Nkrumah, Dr.L.Masschelein-Kleiner (paint medium analysis), and J.P.Kuhn (photodocumentation).

Translated by Walter Newman.

TREATMENT OF A GREEK THIRTEENTH
CENTURY MANUSCRIPT

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5th Triennial Meeting

Zagreb, 1978



TREATMENT OF A GREEK THIRTEENTH CENTURY MANUSCRIPT

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In December 1976, the Central Scientific Research Laboratory for Conservation and Restoration of Museum Artistic Works (WCNILKR) received for treatment a Greek 13th century manuscript, the so-called Nicomedian Gospel from the Scientific Library of the USSR Academy of Sciences in Kiev. It was supposed to appear at the Moscow Exhibition of Byzantine Art in the summer of 1977.

In short, the history of the manuscript is as follows. In 1880 it was purchased by the Church Archaeological Society of the Kiev Theological Academy from a Kiev citizen who, in his turn, had happened to buy it from a Bulgarian said to obtain the Gospel in Nicomedia whereof its name originated (1).

The in-octavo manuscript contains the text of the four Gospels with some minor losses (all in all, 325 leaves survived). Twenty four miniatures of the Gospel evoke modern researchers' major interest. According to its previous owners it was known to contain four more miniatures lost later (2).

The manuscript is written on yellowish, very smooth parchment of medium thickness. At the beginning of the 20th century the Gospel was bound up in soft cardboard covered with green cotton fabric. The original binding, noted indirectly in the articles drawn up by the first researcher of the Gospel, N. Petrov, seems to have disappeared by now without leaving any trace (3).

The parchment of the manuscript was severely deformed while poor binding made it more grievous; miniatures were marked with numerous flakings of the paint layer which is generally typical for Greek handwritten books. The manuscript was evidently in need of urgent conservation measures not only to make its display at the Exhibition possible but also to keep it from further deterioration.

Treatment of the Nicomedian Gospel included all kinds of conservation methods adopted for manuscripts: reinforcement of miniatures, strengthening and "mending" the parchment, preparing a new binding (the old one being impossible to use). Besides, the manuscript's unstitching opened broad prospects for making researches and examination of the miniatures.

The unstitching of the manuscript was the first stage of its treatment. The old binding was easily removed exposing the spine covered abundantly with dry joiner's glue. This, undoubtedly, contributed to the deformation of parchment. The removal of the dry joiner's glue turned to be a painstaking operation. Plenty of glue was spread over not only badly stitched gatherings but also separate torn-off leaves with missing fragments and disrupted folds. To remove a thick and dried-up layer of glue with minimum damage to the parchment, moisture compresses had to be applied to the spine to soften the glue before gradually taking it away with a scalpel.

While unstitching the order of leaves in each gathering was expressed graphically as accepted in palaeography. Such an arrangement subsequently used to alleviate sorting of gatherings since though most of them consisted of eight leaves (combining four doubles) many single ones were sewn in suitable for

folding them in either way. There were as many as twelve leaves in some gatherings (particularly in case of separate pages with miniatures and without the text).

Leaves with miniatures requiring special treatment were separated from the unstitched gatherings in the first instance. The rest of them were cleaned from any surface defilement with an eraser and scalpel; the remnants of dry joiner's glue were also removed from the folds. All the parchment text leaves, overdried, deformed and covered with numerous tiny folds, required softening and straightening out. To this end, a "distance moistening" method accepted by our Laboratory was applied. Damp but well wrung out gauze was covered with capron fabric and a deformed parchment leave spread over. The whole set was overlaid with polyethylene film and plexiglass on top of it used as a light press. Depending on the deformation degree and thickness of the parchment under treatment the moistening process lasted from twenty to fifty minutes (if the gauze dried up while the parchment was not amply moistened it had to be damped once again). When the parchment was sufficiently moistened it was placed under the press with felt packing on both sides. After such treatment the parchment becomes not only smooth but also flexible and, in our opinion, does not require any additional efforts to soften it (for example, injection of lanoline, spermaceti, etc.). Subsequent state of the parchment is subject to its future preservation conditions only.

After the straightening-out procedure it was necessary to clean up such deficiencies as ruptures and frays prevailing at the folds (as a result of sizing the spine of the manuscript while binding). Patches

and amendments were made in this case of new parchment pasted with a parchment glue of 5-6 per cent concentration.

Leaves with miniatures on them required a more thorough approach. The paint layer of some of them (particularly, in three frontispieces) practically scaled off completely. Losses of paint layer in other miniatures painted on smooth parchment or on gilded background averages from one third to 50 per cent of the total surface area. In spite of that miniatures of the Nicomedian Gospel are quite a remarkable artistic phenomenon and their deterioration process is certainly ought to be stopped.

The paint layer was treated with one of the materials used by WCNILKR to this effect: water dispersion of vinyl-acetic copolymer with 2-ethylhexilacrylate of 3-5 per cent concentration (VA 2EHA) (4). Preference was given in this case to the material for the following reasons: the dense paint layer of the miniatures was peeling off in small fractions, but it was not pulverized, and so need not be impregnated by adhesive in other words introduction of disappeared binding media was not required. The only thing left to do was to fix the flaking fragments. VA 2EHA with its strong adhesive properties turned to be the most appropriate substance. It was applied with a thin brush under the edges of destroyed sections. The work was all the time carried out under the microscope. When the reinforcement of the paint layer was over the leaves with miniatures were straightened out by the aid of "distance moistening" and patches were made wherever it was necessary.

Many challenges were faced when solving the problem of a new binding for the manuscript. There was no

sence in utilising the old cardboard cover not fit at all to provide favourable conditions for preservation of straightened-out parchment leaves which were bound to deform once again if left without sufficient pressure directed over them. Apart from problems of esthetic nature (what particular outward appearance should a Greek manuscript of the 13th century have) to accept a purely technological challenge was of major importance, i.e. to rebind the manuscript without sizing its spine and to stitch its gatherings using a method by instrumentality of which no deformation of leaves is caused. Having made a few imitations using various methods of stitching separate gatherings the most suitable variant was chosen and a new covering was produced made of leather-covered boards with two fastenings (5).

x x

x

Examination of miniatures is the most exciting endeavour generally accompanying the treatment of illuminated manuscripts. When a manuscript is unstitched providing a chance of bringing miniatures face to face to compare these artistic samples rather than their reproductions, lots of valuable information may be obtained which is impossible to do while making studies of painting in a stitched, undisjoined manuscript. Miniatures of the Nicomedian Gospel have been thoroughly examined visually by means of a magnifying glass or a microscope, macrophotographs of some details have been made, all the miniatures have been X-rayed and many pigments have been radiophasically analysed. These efforts have resulted in a number of observations pertaining to artistic and technological peculiarities of Greek master craftsmen.

In visual comparison of all twenty four miniatures of the manuscript it becomes evident that they were produced by several craftsmen, possibly by seven or eight of them. It is interesting to note that every group of miniatures painted by one and the same artist is distinguished not only by the same palette (that is by application of some definite pigments which was in a large measure proved by radiographic analysis (6)) but also by a similar nature of distortion, in this case nearly identical "silhouette" of scaled-off fragments.

Unfortunately, radiographs of poorly preserved miniatures of the Nicomedian Gospel failed to fully demonstrate various painting devices of the Greek artists thus making undistinguishable one craftsman from another. But in those cases when painting was preserved in larger fragments some information on that score was, however, gained. Thus, close examination of radiographs made of four ornamental head-pieces furnishing the beginning of every Gospel (depicting Christ Emmanuel in a medallion) has proved the fact that they were produced by four different artists despite superficial resemblance in their pattern, colouring, composition and ornamental nature. In several tests radiographs helped to confirm the assumption that the artists had used different paints for exactly the same purposes: for example, nimbi against a golden background were painted in some cases with cinnabar (and, consequently, they are clearly discernible on the radiograph) while in other cases with a red organic pigment (and, therefore, leaving the nimbi undetectable) (7).

Restoration and examination efforts involved in dealing with the Nicomedian Gospel, an extremely inte-

resting monument of medieval Greek art, have combined the work of a number of specialists: restorers of various specialisations, art historians, palaeographers, physicists. In future we expect to publish materials featuring this work.

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- (1) See bibliography in the catalogue of the exhibition "Byzantine Art in USSR Collections". ("Искусство Византии в собраниях СССР", т. 3, М., 1977, с. 22).
 - (2) N.I.Petrov supposes that the missing miniatures were painted on separate leaves and indicates the number of leaves where these miniatures could be interpaged. (Н.И.Петров. Миниатюры и заставки греческого евангелия XIII века. (Miniatures and headpieces in the thirteenth century Greek Gospel). - "Искусство", Киев, 1911, № 4, с. 186-187). Soviet scholar of Byzantine history, I.S.Chichurov, put forward an idea that some of the missing miniatures were painted on text leaves proceeding from the losses of the text.
 - (3) Н.И.Петров, *ibid.*, с. 187.
 - (4) Г.З.Быкова, И.П.Мокрецова. Средневековая книжная миниатюра на пергаменте, ее сохранность и реставрация. (G.Z.Bykova, I.P.Mokretsova. Medieval miniature on parchment its conservation and restoration). - "Сообщения ВЦНИЛКР", 1970, вып. 26, с. 71; А.В.Иванова. Применение синтетических полимеров для укрепления средневековых миниатюр на пергаменте. (A.V. Ivanova. Application of synthetic polymers for reinforcement of medieval miniatures on parchment). - "Сообщения ВЦНИЛКР", 1975, вып. 30, с. 8.

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- (5) In future we suppose to continue our efforts in solving the problem of restoring medieval bindings and reproducing old samples for manuscripts with destroyed bindings.
- (6) Radiophasic analysis of pigments was carried out by Dr. M.Naumova, scientific worker of the Laboratory.
- (7) X-raying of the miniatures was carried out by V.Ivanov and V.Lukyanov of the Scientific Examination Techniques Department of WCNILKR.

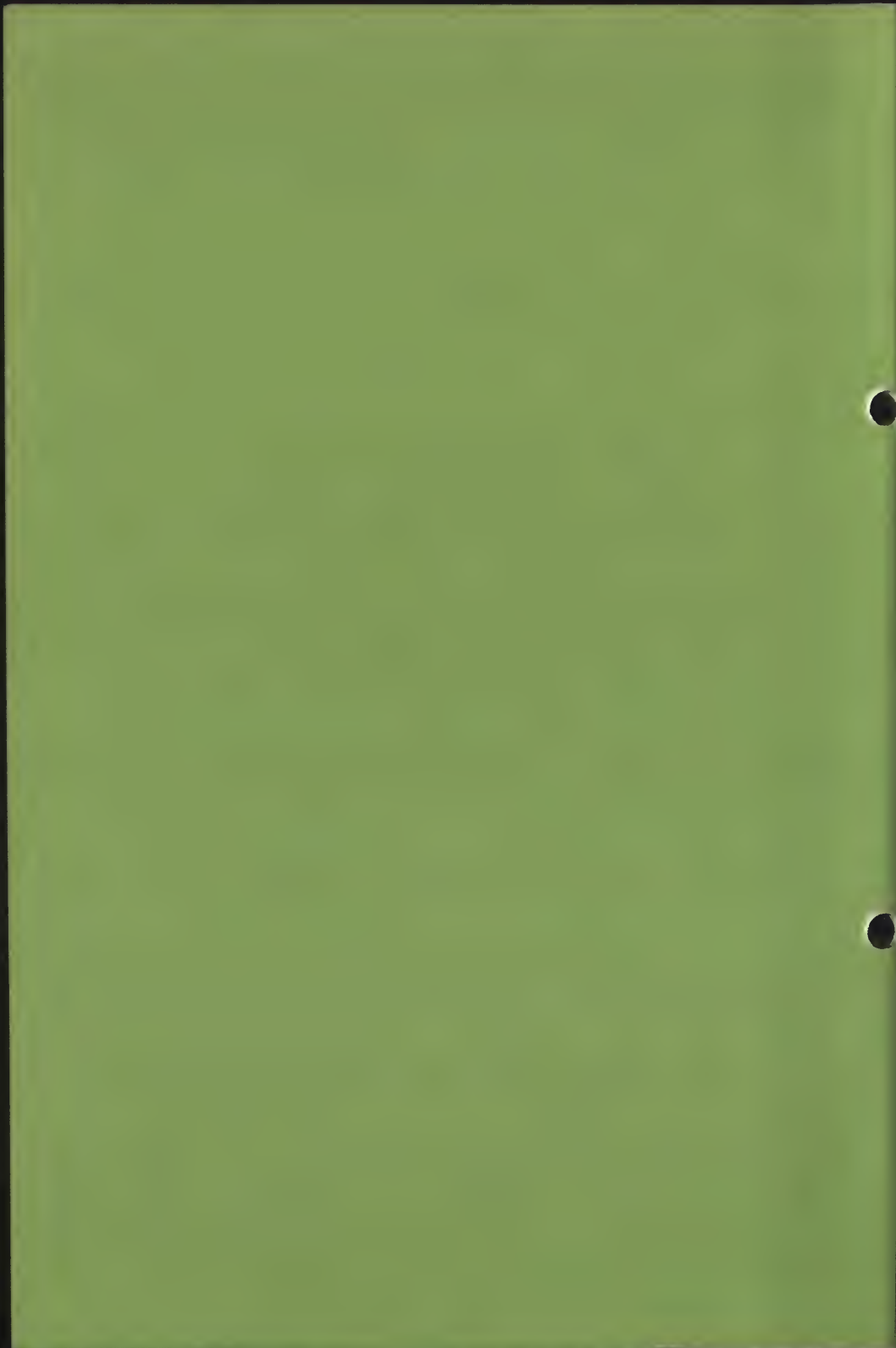
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MESURE D'INTERVENTION EN CAS DE DESASTRE
OU CREATION D'UN CENTRE NATIONAL
D'INTERVENTION ET DE SAUVETAGE EN CAS
D'URGENCE

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Zagreb, 1978



MESURE D'INTERVENTION EN CAS DE DESASTRE OU CREATION
D'UN CENTRE NATIONAL D'INTERVENTION ET DE SAUVETAGE
EN CAS D'URGENCE

Ljiljana Stanojlovic

Notre Service de Restauration, en outre de ses activités habituelles de sauvegarde des documents publics et privés conservés aux Archives nationales du Québec, a dû concevoir un mode de traitement d'urgence des documents du Palais de Justice de Québec, suite à une inondation causée par le gel des conduites d'eau de l'édifice en hiver 1975.

Notre intervention nous a fait constater un évident manque de préparation à combattre les effets d'une catastrophe chez les responsables de nos institutions culturelles. En effet si l'on connaît bien les mesures de prévention contre les éléments destructeurs les plus courants, on s'est peu préparé à affronter avec le plus de succès possible les désastres imprévisibles.

Nous croyons donc pertinent de proposer la création de "Centres nationaux d'intervention et de sauvetage en cas d'urgence". A la fois organismes de sensibilisation et d'intervention, ces centres, dotés d'un personnel qualifié et responsable, éviteraient l'arbitraire des opérations désordonnées.

La bibliographie des ouvrages sur les bâtiments d'archives, les musées et les bibliothèques qui proposent d'importants chapitres sur les mesures préventives contre les incendies et les inondations s'allonge constamment. Les dépôts d'archives, comme les musées et les bibliothèques, visent de plus en plus aux conditions maximales de sécurité et plusieurs atteignent même la perfection à cet égard. Pourtant les désastres naturels ou ceux qui sont causés par l'homme demeurent inévitables et aucun système de prévention, quelle que soit sa perfection, n'est infaillible. Qu'on se rappelle les ravages causés à Florence (Italie), à Corning (Etats-Unis) et à Fort Williams (Canada).

Si les théoriciens et les patriciens des bâtiments à vocation culturelle ont pu réaliser jusqu'ici des aménagements tout-à-fait sécuritaires, je me demande si nous sommes suffisamment préparés à affronter les conséquences d'une catastrophe imprévue et soudaine. La surprise et le désarroi en entraînant le désordre, l'imprudence et l'inefficacité risquent d'être autant dommageables que le désastre lui-même.

Permettez-nous de vous relater une expérience récente vécue par nos services:

Au mois de février 1975, un froid exceptionnel couvrit le Canada et particulièrement le Québec. Il provoqua par le gel le bris des conduites d'eau au vieux Palais de Justice de Québec où logeait le Bureau d'enregistrement. En quelques minutes, plus de 80 centimètres d'eau glacée envahirent le Service d'archives situé au sous-sol et inondèrent complètement les 105 volumineux registres et les 75,000 documents qui y étaient conservés.

Au Québec, le Bureau d'enregistrement reçoit tous les actes de mutation de propriété. Ainsi conserve-t-il les actes notariés et les testaments olographes de même que les dossiers de recherche et les copies d'enregistrement. Par leur nature, ces documents sont absolument uniques et irremplaçables de même qu'essentiels aux opérations courantes de la Justice puisque seuls garants des titres de propriété. Ces documents inondés couvraient les années 1850 à 1950.

Or, par imprévoyance ou ignorance des soins d'urgence à apporter, on a prévenu les Archives nationales du Québec une semaine après le désastre. Une semaine

au cours de laquelle les documents ont trempé dans une eau immobile et boueuse à cause de la poussière accumulée depuis des années. Un heureux hasard a tout-de-même voulu que les documents ne soient pas dispersés puisqu'ils étaient enfermés dans des tiroirs métalliques ou des boîtes cartonnées.

Nous avons immédiatement ordonné l'évacuation du dépôt. Chaque tiroir de même que chaque registre fut emballé et immédiatement congelé. On transporta dans des camions frigorifiques tous ces documents à Montréal à proximité de notre laboratoire de restauration où on les entreposa dans d'immenses congélateurs loués pour l'occasion.

La restauration proprement dite allait pouvoir enfin commencer. Quatre difficultés d'importance se sont dès lors posées:

- 1- Le long séjour des documents dans l'eau glacée et sale avait provoqué l'apparition de moisissures, nous obligeant à une opération de désinfection indispensable.
- 2- Nous n'avions pas encore d'autoclave (vacuum desinfection chamber) pour procéder au séchage et à la fumigation massive des nombreux documents avariés.
- 3- Nous ne disposions pas non plus d'un personnel de soutien expérimenté pour ce genre de travail.
- 4- Il était enfin urgent de remettre en bon état les registres de renvoi des dossiers d'enregistrement pour les fins de l'administration de la Justice.

Au surplus pour ajouter à ces difficultés, une expertise archivistique et juridique nous informa que tous ces documents étaient bel et bien uniques et essentiels. En outre, en l'absence d'un équipement de laboratoire adéquat, ils allaient devoir être séchés, nettoyés, désinfectés et restaurés manuellement et ce dans les plus brefs délais pour ne pas nuire aux opérations judiciaires et aux recherches des notaires.

Les registres furent traités en premier. Par demi-douzaine, nous les avons placés debout sur des soutiens variés, en demi-cercle devant de puissants ventilateurs distants d'environ 3 mètres. Nous ne pouvions en effet les suspendre sur des fils d'acier

ou des cordes de nylon puisqu'ils étaient trop volumineux et trop lourds, étant totalement imprégnés d'eau. Cette disposition accentuait autour des registres la circulation d'air nécessaire à leur assèchement.

Pendant ce temps, nous préparions des centaines de feuilles de papier journal non imprimé et de papier buvard. Ces feuilles trempées dans une solution de thymol (10%) et d'alcool 96 degrés (90%) allaient être insérées entre les pages des registres, au préalable suffisamment égoutés pour être ouverts, et changées aux trois ou quatre heures. Nous avons ainsi asséchés tous les registres, en comptant cinq à huit jours pour chacun selon son épaisseur.

Après le séchage complet de chacun des registres, nous les nettoyions avec la même solution de thymol (10%) et d'alcool (90%). Enfin dans certains cas, nous avons dû corriger l'ondulation des feuilles de certains registres en les plaçant sous presse quelques heures. Dans les cas où les couvertures étaient endommagées, notre service de reliure a pu les réparer ou les remplacer. Par ce procédé simple et lent, nous avons réussi à sécher, nettoyer et désinfecter tous les 105 registres que nous continuons à inspecter périodiquement au Palais de Justice de Québec où ils ont été retournés. Heureusement aucune tache de moisissure n'est réapparue.

Le traitement des pièces détachées, actes notariés et autres, posa des problèmes différents. Comme nous l'avons vu précédemment, nous les avons entreposées dans des congélateurs dans des contenants bien identifiés correspondant aux tiroirs de conservation de leur dépôt d'archives d'origine. Pour les décongeler, à la fin de chaque journée, nous disposions trois à quatre paquets de documents dans les bassins du laboratoire. Le lendemain matin, chaque document pouvait être traité.

Après avoir été lavés, nettoyés et même dans certain cas déacidifiés, les documents étaient placés dans un séchoir pouvant contenir plusieurs centaines de feuilles. Lorsque leur humidité atteignait environ 15 à 20%, nous les désinfectons en plaçant chaque feuille entre deux buvards imprégnés de la solution thymol-alcool dans une proportion de 10/90% puis en les comprimant légèrement dans notre presse.

Ce traitement simple devait se compliquer lorsqu'il a fallu remettre les timbres-fiscaux à leur place d'origine sur chacun des documents. En effet au cours de l'inondation prolongée et pendant la décongélation, les timbres-fiscaux apposés sur les documents ont été décollés et dispersés. Ils pouvaient être nombreux sur un même document. Fallait-il ignorer ces timbres épars ou les remettre à leur place? Les avis juridiques étaient divergents; les uns concluaient à l'égale valeur des documents avec ou sans timbres, les autres craignaient que l'originalité et l'authenticité des documents puissent être contestées sans la présence des timbres-fiscaux d'origine. Nous avons donc opté pour la remise des timbres-fiscaux à leur place sur les documents; votre expérience vous dira la somme de travail ainsi nécessitée.

Cette expérience que nous avons vécue presque par hasard, nous a porté à déplorer tous les cas de désastres qui ont pu survenir sans qu'aucune personne avertie en ait été prévenue. Le délai d'une semaine qui s'est produit entre l'inondation et le recours à nos services et ce, à l'intérieur d'une même administration publique, permet d'imaginer toutes les pertes qu'ont du subir les organismes publics et privés de même que les particuliers aux prises avec des problèmes urgents de conservation et ignorant jusqu'à notre existence. Ce problème n'est pas seulement québécois, il est mondial.

Si, comme nous l'avons vu plus haut, les mesures de prévention sont généralement connues, peut-on en dire autant des mesures de combat qu'il est urgent de mettre en oeuvre lorsque surviennent des catastrophes? Nos discussions avec plusieurs conservateurs de services d'archives, de musées et de bibliothèques confirment nos inquiétudes. Si la plupart d'entre eux connaissent bien l'existence de nos laboratoires, personne ne connaît l'existence d'un service d'assistance professionnelle en cas de désastres.

C'est pourquoi il nous a semblé intéressant de réfléchir avec vous sur la possibilité de créer dans nos pays un "Centre national d'intervention et de sauvetage en cas d'urgence".

Créer sur une échelle nationale, ce centre regrouperait du personnel volontaire issu de nos diverses institutions culturelles. Composé de représentants de plusieurs disciplines de la documentation, il serait

en mesure d'élaborer un ensemble de procédures, dans les plus brefs délais, pour faire obstacle à la détérioration de nos richesses patrimoniales, victime d'une catastrophe. Il lui appartiendrait en effet d'organiser, de diriger et de surveiller les opérations de sauvetage de même que d'effectuer le travail urgent de récupération et de restauration.

Cette équipe de spécialistes pourrait être mobilisée en hâte pour aller aider les conservateurs de services d'archives, de bibliothèques ou de musées placés subitement devant des difficultés imprévisibles. Il va de soi que de telles interventions ne sauraient être réalisables sans un programme développé de sensibilisation auprès du personnel de nos institutions et auprès du public en général.

Voici, à notre avis, quelques instructions de base qui pourraient être utiles aux organismes ou aux particuliers susceptibles de recourir aux services d'un "Centre national d'intervention et de sauvetage en cas d'urgence".

- Localiser au préalable le ou les magasins les plus rapprochés pour l'achat de matériel de sauvetage.
- Localiser au préalable une chambre froide (camion ou entrepôt frigorifique) pour permettre la congélation immédiate des documents avariés.
- Dès la constatation du désastre, appeler immédiatement le "Centre national".
- Mentionner si, parmi les documents, se trouvent des photographies, films et diapositives.
- Ne pas toucher aux documents avant l'arrivée des représentants du "Centre national".
- En cas d'incendie, insister auprès des pompiers pour qu'ils assurent en priorité l'accès à l'institution victime.
- En cas d'inondation, ouvrir toutes les fenêtres pour permettre une circulation optimale de l'air.
- Recruter un nombre suffisant de personnes de soutien pour permettre l'évacuation rapide des lieux affectés.

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- Ne pas essayer ni d'ouvrir, ni de fermer les livres et documents mouillés ni d'y inscrire quoi que ce soit.
- Recruter des moyens de transport pour accélérer l'évacuation.
- Si les documents sont dispersés, assurer la présence de tous les professionnels de l'institution victime pour fins d'identification.
- Les lieux affectés doivent être vidés de leur contenu le plus rapidement possible selon les instructions et sous la surveillance du personnel du "Centre national".

Nous espérons, chers collègues, que ces brèves remarques sur un aspect quelque peu négligé de notre profession sauront être approfondies par vos expériences respectives de sorte qu'un jour naîtra peut-être un premier "Centre national d'intervention et de sauvetage en cas d'urgence". Pour notre part, nous comptons présenter ce projet, enrichi par vos commentaires, à notre Directeur général des Archives nationales du Québec, monsieur François Beaudin qui a eu l'extrême obligeance de me permettre de venir vous en entretenir et que je remercie vivement.

Merci de votre attention.



CHINESE DRAWINGS FROM THE COLLECTION
IN THE POLTAVA ART MUSEUM

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5th Triennial Meeting
Zagreb, 1978



CHINESE DRAWINGS FROM THE COLLECTION IN THE POLTAVA ART
MUSEUM

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Our study and restoration of Chinese drawings is a continuation of the immense amount of work we have done over a number of years on the restoration of oriental paintings on silk and paper. First to be tackled was the problem of restoring Chinese prints; then came the problem of restoring oriental paintings (Chinese and Japanese scrolls) on silk and paper; and lastly the problem of restoring Chinese drawings on paper.

If we consider what a large number of exhibits from the Orient there are in the museums of the Soviet Union, it becomes clear that this problem did not arise accidentally. Moreover, it was the experience gained during the restoration of various types of European drawings that made its solution possible (9).

A few years ago thirty-nine so-called Chinese miniatures of the 19th century were sent by the Poltava Art Gallery to the Grabar Russian National Research and Restoration Centre for Works of Art with a request that they be restored. These miniatures were executed mainly in gouache on thin, silky, soft, easily damaged paper. Nearly all of them were stuck on to thin Chinese rice paper, and had strips of raised coloured fabric stuck along the edges, forming a kind of coloured framework, the whole being set in a black wooden frame under glass (as was the custom at the time).

It was apparently the smallness of the drawings that led to their being called miniatures. However, not all of them correspond to the usual understanding of that term from the artistic point of view, that of a very small painting with specific finesse in the man-

ner of execution. Thus they should more properly be called simply drawings.

Such drawings, nevertheless, are of a certain interest from an instructive point of view, since they show various aspects of the life and ways of the Chinese people, and specific traits in the work of Chinese artists. They portray Chinese men and women walking, or sitting, or playing musical instruments; scenes of games, conjuring, punishments, and so on. Some of them are drawings by craftsmen, who often made their paper themselves, then made the drawings and sold them then and there, at the gate, to foreign tourists. Some of these drawings, more especially pieces depicting plants, butterflies and beetles, are done extremely professionally.

The state of conservation of the drawings was such as to require serious attention. They were yellowed; dust had eaten into them; they were dirty, covered with stains and scratches; they were torn, and had pieces missing; and they were backed by flimsy, deformed paper that could not withstand wear and tear. Of the many tasks arising from the necessity to restore these drawings the key one was to make a careful study of the paper, to find out what it had been made of, and to decide what materials and techniques to use in order to obtain optimal results. It was on this that the whole restoration process depended.

It was sufficient to make a thorough visual examination to draw the main conclusion: that the paper used for the drawings was an unusual kind, requiring careful study and the elaboration of special methods of restoration.

The first stages of the investigation revealed the specific texture of the base of the drawings, which is characterized by a softness, airiness and looseness;

yet the paper is at the same time extraordinarily brittle and cracks easily. There is a kind of stripe or band running up and down the paper, which is more noticeable in some drawings than in others. There are also traces of netting (possibly of silk).

A visual examination of the paper under a binocular magnifying glass and a test of its fibre content led to the conclusion that the composition of this paper did not conform to the generally accepted notion. Presumably it was prepared from the pith of a plant.

Many different materials are known to be used for paper-making in China, and it is due to this that there is such a large variety of types. Chinese paper may be made of bamboo (Sun In-Sin: "Book on the Chinese Method of Making Paper"), cotton, scraps of silk, straw, certain kinds of grass, such as Chinese Bumeria

(the Chinese nettle or, as it is also called, Chinese hemp), the Chinese Liviston palm, the cyprus, cottonwood (*Broussonetia papyrifera*), the Chinese tree (*Tetrapanax Papyrifer*) and others.

In answer to a request for information, the laboratory of the Moscow State University Botanical Gardens, we were told that an anatomical analysis of the paper used for painting in China in the 19th century (a sample of which we had sent them) showed it be rice paper made from Chinese cottonwood, or *Tetrapanax Papyrifer*.

Now that we had established what material the paper was made of, one of our important problems was solved. However, the appellation of the paper seemed dubious. If it was called rice paper, what could we call the other kind that we had long been accustomed to call rice paper? And it was this other kind that had served the Chinese drawings we have been discussing as a backing. The two kinds of paper are very

different both in appearance and inner structure.

The copious literature in the Soviet Union on the history of paper, its production, classification, characterization, etc., gives very little information about Chinese paper in general and Chinese rice paper in particular. What information exists, is scrappy, sometimes contradictory, and occasionally confused. One author (1) speaks of Chinese paper as being made of young bamboo shoots, bass from the mulberry tree and so on. Another (6) only speaks of the great difference between Chinese paper made of silk and bamboo fibre from the European kind made of hemp and flax. A third (7) does not name the material that the paper is made of, but says that Chinese hand-made paper, only one side of which is used for painting on with a brush, is very strong, and preserves its original appearance for centuries. A fourth (10) refers to Chinese paper made of cottonwood (*Broussonetia Papyrifera*).

We shall not cite other authors who add little to what has already been said; we shall only discuss those that deal with the paper that is of interest to us. Thus, in an encyclopaedic dictionary called "Granat" (16), we find that paper made of the pith of the *Aralia Papyrifera* is called rice paper (!), and that this paper, like papyrus, differs greatly from modern paper, being a sheet from 0.02 to 0.3 mm. thick, made of matted fibres (?!).

The most complete answer to our question is given in two books (2,3), in which the paper is called "so-called rice paper". These books mention its use in watercolour painting, in making artificial flowers and surgical bandages. They also give its synonyms, its local names and the places where the *aralia* grows.

Not long ago we came across a book that without dealing specifically with the problem in question, gives a detailed description of how this particular kind of paper is made (13).

Thus, basing our conclusions on published works, and a number of laboratory data obtained by visual examination under a binocular magnifying glass and in filtered ultra-violet rays, by testing the fibre composition of the paper, pH, the (paste used to stick the drawings on to the mounts, by analysis of the paints, analysis of the humidity of the paper on which the drawings were made and the backing, macrophotography, photography in reflected ultra-violet rays, in luminescence in ultra-violet rays, and photography in infra-red rays, we have been able to establish:

1. The paper on which the Chinese drawings from the collection in the Poltava Art Gallery were executed is made of *Tetrapanax Papyrifera*, or *Aralia papyrifera*.

2. The appellation "rice paper" is incorrect.

3. To make the paints for the drawings mineral pigments and whitelead were used.

4. The specific nature of the technique used in this kind of painting was discovered.

5. A description has been found of the method by which paper is made from *Tetrapanax Papyrifer*.

It was only after this research was carried out and the conclusions we have mentioned were reached that it became possible to proceed to a search for the most harmless way of restoring the drawings.

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As a result, the bulk of methods hitherto accepted in our practice for the restoration of objects of cultural value were revised to suit such exceptionally capricious materials as the paper of the Chinese drawings.

After a large number of experimental tests trials, in which an exact facsimile of the paper was used, and after all the laboratory investigations already mentioned special methods were developed and recorder in the for of directions which, we believe, can serve as guidance in restoring drawings on paper made of Tetrapanax Papyrifer. The method, naturally, is open to further improvement.

All the drawings from the Poltava Art Gallery have been restored in accordance with these directions.

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78/14/5

GOTHIC BINDINGS AND THEIR RESTORATION

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5th Triennial Meeting
Zagreb, 1978



GOTHIC BINDINGS AND THEIR RESTORATION

Endel Valk-Falk

Though the concept of systematic restoration of objects of art and architecture has been in existence for many a decade it was employed in the field of book-conservation considerably later. Until the preceding century, a majority of the libraries belonged to the private sector, as a consequence of which the mode of conservation of books was principally dictated by the individual tastes of the owners. The decaying original bindings of numerous ancient books were replaced by contemporary ones.

In the course of restoration of an un-rebound incunabla - Bernhardus Clarenvallensis' 'Sermones de Tempore et de Sanctis', printed by Perer Schöffer in 1475 - I examined all the publications and their bindings of P.Schöffer's printing house, available at various Soviet libraries. Original bindings have not preserved on these books either at Lenin State Library, Moscow or at Academy of Sciences Library, Leningrad (14 works). A major portion of the incunablas at the Scientific Library of Tartu State University are, as well, rebound in the binding style of the last century. Though further rebinding at a later date has resulted into their obtaining a strong binding which opens well, and for which contemporary materials of high quality have been used, this has been done at the cost of their historical binding characteristics. Frequently, ancient but heavily damaged binding leather and broken boards are replaced with the newer ones, the resulting binding thus becoming a twentieth century binding in 'mediaeval fashion'.

At the initiative of Estonian Restorers' Society, an all-Union restoration seminar was organized at Tartu in November

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1976. This seminar was, for the first time here, devoted to the problems pertaining to binding restoration. The reports and discussions revealed the extent of thorough research work being carried out as well as growth of qualified restoration personnel in the field where, besides achievements in theoretical and chemical spheres, noteworthy results have been achieved in the practical arena. (The reports will shortly be published in 'Raamat, aeg, restaureerimine IV' - 'Book, Time, Restoration IV'). That this seminar was held in the Estonian S.S.R. is logical as this republic has long-established traditions as concerns decorative leather handicrafts, including leather bindings. The works of Eduard Taska, Adamson, Eric, Adele Reindorff and others are internationally well-known. Quite a few of their pupils have specialized in the field of leather restoration.

The largest staff of restorers in the Estonian S.S.R. work at the Scientific Library of TSU (25 restorers) where, in addition to art-historians, chemists and biologists, there are employed a host of artists-binder-restorers. It was the 1966 fire at the library that gave the real impetus to the enlargement of the restoration activities and employment of a larger staff. A further expansion of the department, with numerous laboratories, and with the capability of handling extensive methodical aspects as well as satisfying the requirements of all our national archives and libraries, is foreseen in the new library building, now under construction, with a capacity of five million volumes.

Generally, it is our practice to conserve, over a given period, the ancient bindings of any one specific collection or those belonging to one definite style. A few years ago we began to compile a list of all the incunablas in Estonia from the standpoint of the nature and extent of restoration they required, and began to restore them. 114 books of those printed prior to the year 1500 A.D. have preserved in the Estonian S.S.R.: 42 of these are stocked at the Scientific Library of TSU, 43 at

the Scientific Library of the Estonian Academy of Sciences, 18 at Tallinn Central Archives, 4 at Fr. Kreutzwaldi State Library and 2 at State Historical Museum. As the list has been compiled on the basis of the characteristics of the original bindings, the number of punched cards does not concur with the number of incunabla-bindings. (Some of the incunabla-bindings are to be considered, from the standpoint of binding history, as belonging to the 19th century, since, on account of later rebindings, their original binding attributes have not been preserved).

The peculiarities of the mediaeval bindings have resulted from the nature of practical demands of handling made on the books at the time. Evangelium was not read at homes but at churches where it was worshipped as a symbol of religious services. Of necessity it, therefore, bears an imposing design, is heavy in its structure and is always arranged in a particular position on the lectern. A bulk of incunablas that have preserved their original bindings have wooden covers with large round bosses and in folios (*libri catenati*) with iron chains. Since the printing houses could not adequately satisfy the demand for books at the time, the latter were required to be transported in loose sections to various centres, where the local binders provided them with bindings as per the desires of their customers. In the second half of the 15th century, the activities of the travelling binders were intensified. They worked in the rooms provided to them at the monasteries. The required materials for the purpose - clasps, fillets, rolls, pallets, etc. - were imported similarly from larger centres. As a result Gothic bindings do bear specific compositions; however, different ornamental stamps and rolls were prepared at different places due to the fact that preparation of metal dies for such stamps and rolls, and hand-tooling of coins had achieved a considerably superior level of craftsmanship.

What role did the mediaeval Tallinn play as to the history of book-making? Surrounded by a fortress-wall 15m high, and which is reinforced by 28 defence towers, it surpasses Nuremberg, Cologne and Visby fortress-walls in height and defence potential. Tall above other buildings, there rise in the town the Virgin Mary Cathedral (1233), Church of St. Olev (1267), Church of St. Nicholas (1316), Holy Christ's Church (1316) and the Town Hall (1340). The market square adjacent to the Town Hall is bristling with brisk trade. Every third day a ship anchors at the port with a cargo of silver, salt, textiles, herrings, tin, iron, copper, wines, tanned leather and books. The ships from Novogorod bring grains, fur, linen, mustard, tar and wax. The candles prepared from Russian wax provide lighting to all Northern Europe. As a centre of transit commerce and a member of the Hansa Guild, Tallinn rises to a position of prominence amongst the cities along the shores of the Baltic Sea at the beginning of the 16th century.

Commerce as well as the then-existing schools - the Dome School (1319), the Dominican Monastery School (1413) and the school at the Church of St. Olev (1428) - required books to fulfill its activities. The civic register of the town (1409-1624) lists, besides the vocation of chamois and Cardova leather tanners, that of the binder. The catalogue (1552) of the library of St. Olai's Church has registered receipts of the books: 'aus der Bibl. den Nikolaikirche' and 'aus der alten revalscher Bibliothek'. Later archaeological excavations at the Dominican Monastery and St. Brigitte Monastery sites have yielded numerous finds pertaining to writing materials and fillets, rolls and pallets as well as bosses from book-covers, which amply goes to demonstrate the fact that the craft of binding was cultivated in mediaeval Tallinn. The life-time of the books extant to our days extends to approximately five centuries. Thanks to the well-executed and strong bindings, the text-blocks have been well-preserved over this lengthy period. What are the principal

defects that accrue to Gothic bindings and how have the latter been conserved by Estonian restorers?

Damaged Wooden Covers. These are re-inforced, when broken, by adhering them together and bevelling the joint; the latter, or when the boards are cracked, the crack is then covered with strong long-fibred or rag paper. For these and for repairing all defective wooden boards, dry ones of the same kind and direction as the original ones should be used. In case of insect damage, the holes etc. are filled with a paste made of polyvinylacetate and finely ground wood meal and the deformed wooden boards are treated with wax cream.

Bindings with Weakened Spines can be reinforced with a new back-lining of leather, parchment or batistè. Loose book-sections may be attached by stitching them through the re-inforcing cloth. The covers of very tight-backed books should be loosened to open-up the spine a little.

Prior to Re-sewing the Text-Block, we wax the binding thread in order that it would prevent the glues and adhesives from penetrating into the thread. In re-sewing the text-block, the original method of sewing is meticulously adhered to. This is previously recorded in the form of a drawing (Diagram).

Reinforcing the First Sections by addition of a paper or leather strip joint, in width a quarter of the width of the section; in case of rounding a book it is kept unglued between the sections until the rounding is finished.

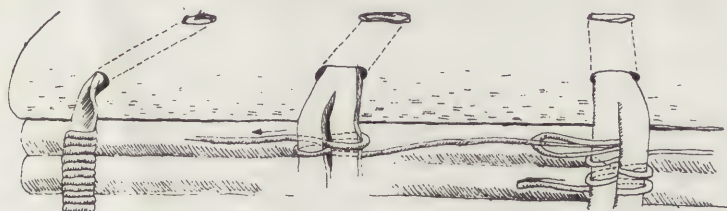
Restoration of the Damaged Pages within a bound book by wet-treatment without causing any damage to the backbone or the spine is possible by employing batik technique. If the sections get stretched beyond their original size they should not be trimmed.

New Headbands are made precisely resembling the original ones in every detail - technique, material and the colours. In the 15th century bindings, three types of headbands are to be found:

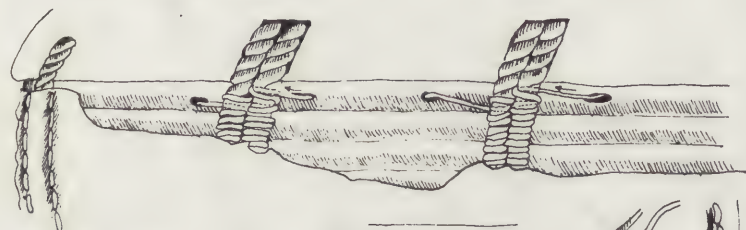
leather bands or hemp threads join the ends of the spine to two covering boards which are covered with leather and sewn through the leather of the spine. The second kind are the interlaced leather-band headbands, which are fixed to the kettle-stitch with the aid of long stitches (Diagram). The Greek-Slavonian bindings have the headbands beginning at the edges of the bindings' covers and extending over the text-block in relief. Armenian-Orient bindings have textile bands in diverse colours, which are fixed on a section of the text-block. Softening Ancient Vegetable-tanned Leather with nutritious cream prepared from mineral oil, beeswax and thymol used as an antiseptic. Parchment and white leather are cleaned with neat's bile emulsion.

Small Missing Portions of Covering Leather is replaced with new, hand coloured vegetable-tanned calf-skin, on which the principal lines of the existing design are extended. If the leather is entirely missing, I have used, for re-construction of the design, the relief lines of the design preserved on the wooden surface of the covering boards. Pencil-copy of these made on a transparent paper enables one to derive a general design on the lines of the original one. This, either from a zinc-die or by hand, when impressed upon the new leather, imparts an outline of the original design.

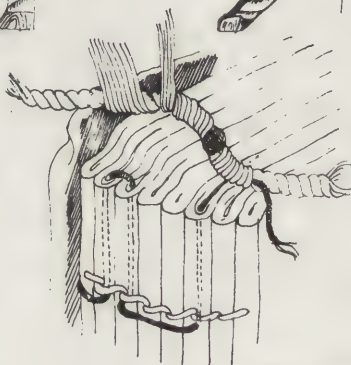
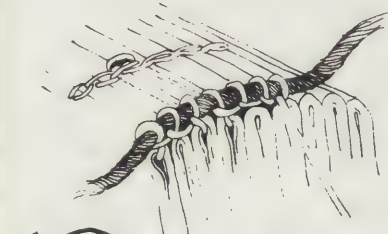
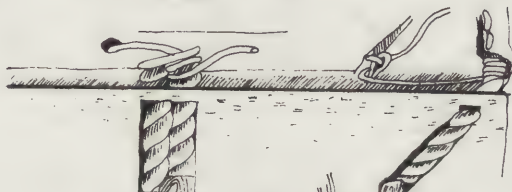
Wooden covers of Gothic bindings possess scores of characteristics very peculiar to the style, attentive and unaltered preservation of which in the course of restoration ensures the preservation of the rarity of the binding even subsequent to extensive restoration treatments.



ENSV TATR I 2335
PETER SCHOFFER MAINZ 1475



ENSV TATR I 2300
NICOLAUS KESSLER
BASEL 1486



ENSV TATR I 2246
STEPHAN ARNDT LUBECK 1494



78/14/6

PREDICTION OF THE SERVICE LIFE OF
THE PAPER CONTAINING POLYMERIC ADHESIVES

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PREDICTION OF THE SERVICE LIFE OF THE PAPER CONTAINING
POLYMERIC ADHESIVES

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In connection with extensive use of polymeric compounds in restoration practice it has become necessary to determine the stability of the paper-polymer system. It has been discovered that the existing methods of artificial aging of paper containing polymeric additives by heating them cause an increasing in durability and do not have the same effects as natural paper aging.

In the State Public Library a method of predicting the life of paper has been worked out. The method is based on artificial paper aging caused by a mechanical load. The approximate lifetime for papers of different composition containing polymeric additives has been established.

Those working on the preservation of library, archive and museum stocks know well that progress in this field is possible only by introducing synthetic and artificial polymeric compounds. The polymers introduced into the paper of documents restore the properties lost in the process of aging, increase the durability of the paper, make it possible to mechanize the restoration process and simplify the technology, protect the materials from environmental influence. At the same time the researchers, restorers and archive specialists are worried about the permanence and durability of paper containing various polymers.

It is known that the widely used method aging by heat is not applicable to paper with polymer because structurization prevails over destruction in the pro-

cess, which is often expressed in an increase in mechanical indices [1, 2]. The absence of methods to assess the permanence and durability of paper containing synthetic polymers stands in the way of a broader research into new polymeric compounds for paper conservation and restoration and their use.

A method has been developed for assessing the length of life of paper containing synthetic and artificial polymers which is now in use in the State Public Library. This method does not require artificial aging by heat. In the suggested method an attempt is made to take into account both natural aging and mechanical loads which paper is subjected to during storage and extensive use in libraries and archives [3].

This method is based on accelerated aging of paper under the influence of a mechanical load. It is known that repeated or prolonged influence of the load on the material quickens chemical processes in it. A mechanically stressed bond requires less activation energy than an unstressed one for proceeding of chemical reactions, for instance, oxidizing destruction. The mechanism of the process of the mechanical influence is considered to be similar to that of polymer aging under the influence of light and heat and therefore can be regarded as a modification of aging [4].

Prediction of lifetime is based on the kinetic concept of strength suggested by S. N. Zhurkov according to which the lifetime of a specimen under load, i.e. the time necessary for its destruction, is assumed as an evaluation of its physical strength. The fracture of the body is a result of the rupture of single chemical bonds in places of local over stresses under the influence of thermofluctuation. The role of the mechanical stress comes to activation and agitation of ruptured bonds and separation disjoined atoms from each other.

It makes the fracture process irreversible and the bond recombination impossible [5, 6].

For durability evaluation of paper with polymeric compounds a dependence has been used to define the values of an activation energy for the fracture process of different paper either with or without polymers.

According to Zhurkov's concept the lifetime of a solid is expressed by

$$\tau = \tau_0 \exp \frac{U_0 - \gamma \sigma}{RT} \quad (I),$$

where τ - time period from the beginning of loading to the specimen rupture, s ;

U_0 - activation energy of the fracture process, J/mol ;

σ - stress which the material experiences, Pa ;

γ - coefficient characterizing the degree of non-uniformity in microstress distribution in the solid under test, $-\frac{Jm^2}{g-mol}$;

T - temperature, K ;

R - universal gas constant, $-\frac{J}{g-mol \cdot K}$;

τ_0 - value close to the period of atomic oscillation in solids, equal to $10^{-12} - 10^{-13}$ s .

Paper is a weakly orientated heterogeneous material consisting of separate fibres which form a sheet by means of interfibre bonds. In this case one should choose the right kind of the load influencing both the fibres and the bonds between them. The folding endurance test was used as the required loading. This test is known to give the most accurate evidence of paper changing during aging [7]. The measurement was carried out with a device which bended a paper strip at an angle of 90° , the value of static stress being regulated by different loads. In this case a paper specimen was subjected to the influence of static (σ_{st}) and dynamic cyclic loading (σ_d). Their combined action

resulted in the fracture of intra- or interfibre bonds in paper. The total stress which the strip of paper experienced during bending is $\sigma = \sigma_{st} + \sigma_d$ (2).

Assuming the dynamic stress variation sinusoidal and the principle of flaw summation basic equation of lifetime was used. Its transformation has given an expression for durability of paper when folding

$$\lg \tau' = \lg \tau_0 - \lg I_0 \left(\frac{\sigma \sigma_0}{2RT} \right) + \frac{U_0}{2.3RT} - \frac{\sigma \sigma_0}{4.6RT} - \frac{\sigma}{2.3RT} \sigma_{st} \quad (3),$$

where τ' - time period from the beginning of loading to the fracture of the sample, s ;

I_0 - Bessel's function with an imaginary argument;

σ_0 - maximum value of cyclic load during bending, Pa .

To simplify the calculation it was adopted that the temperature of the specimen was the same during fold testing. Besides we had no evidence of any noticeable temperature change of paper.

Formula (3) may be represented as the following linear equation $\lg \tau' = a + b \sigma_{st}$ (4),

where $a = \lg \tau_0 - \lg I_0 \left(\frac{\sigma \sigma_0}{2RT} \right) + \frac{U_0}{2.3RT} - \frac{\sigma \sigma_0}{4.6RT}$ (5),

$$b = -\frac{\sigma}{2.3RT} \quad (6).$$

For determining the energy of activation from equation (3) it is necessary to be sure that the $\lg \tau' = f(\sigma_{st})$ dependance be linear. A diagram was plotted using the results of the paper fold testing for different papers with about 4-5 loads. The stress was equal to the mass of the load relative to the cross-section of a paper strip and lifetime was a double fold number multiplied by the duration of a double fold. Plots received from the experiment for the paper with some polymers represented a straight line in all cases (Fig. 1).

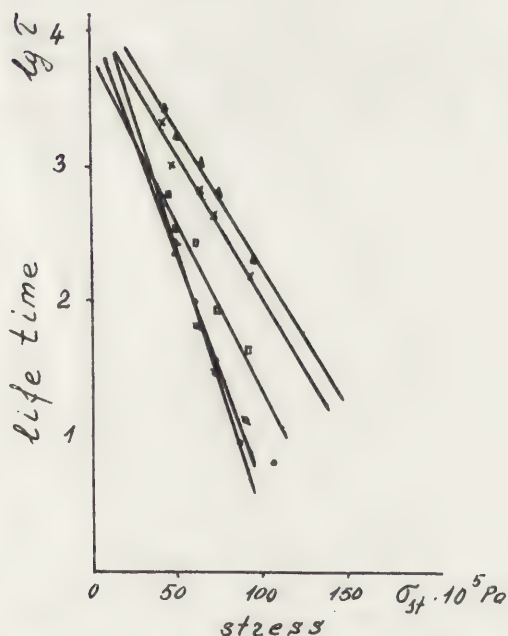


Fig. 1. Lifetime of cotton fibre paper with or without polymers vs. stress under static loads.

- - cotton fibre paper,
- x - the same with polyvinylalcohol,
- - the same with methylcellulose,
- ▲ - the same with NaCMC,
- * - the same with polyvinylacetate

The value of $\bar{\gamma}$ was determined from equation (4) by the method of the least squares and use of experimental data.

For evaluation of $\bar{\sigma}_0$ the dynamic load the following equation was used $\bar{\sigma}_0 = E' \bar{\varepsilon}^{\frac{2}{3}}$ (7), which describes a nonlinear part of the diagram stress-deformation where E - elasticity modulus, Pa ;
 $\bar{\varepsilon}$ - relative deformation.

The value of E was found out from the value of rigidity during bend testing. Relative deformation was determined from the maximum tension which arose during bending in the examined paper section depending on thickness (h) and radius of the bend, curvature (ρ) according to the formula

$$\epsilon = \frac{h}{2\rho} \quad (8)$$

The U_0 value is considered as an activation energy of a destruction process of the paper stored under ideal conditions and not used. In this case paper destruction process is due to thermofluctuations only. The total external effect on paper stored or in the normal use decreases its service life. Assuming that the mechanical force which the paper strip is subjected to during the fold endurance testing with $P = 10\text{ H}$ imitates its deterioration as a result of extensive use, handling and natural aging conditions it would be possible to apply the value

$$U = U_0 - f(\sigma_{st} + \sigma_o) \quad (9)$$

for calculating the paper service life of books and other materials on paper base being constantly used. Lifetime relative value for 2 kinds of papers, for instance, with or without polymeric additives can be determined by the formula

$$\frac{\tau_1}{\tau_2} = \exp \frac{U_1 - U_2}{RT} \quad (10),$$

where τ_1 - lifetime of the paper with polymer, s;

τ_2 - the same without polymer, s;

U_1 - activation energy of destruction process of the paper with polymer, J/mol;

U_2 - the same without polymer, J/mol.

For determining the absolute values of lifetime it is necessary to carry out artificial heat aging of the paper without polymer and calculate the lifetime of paper with polymer by means of the Arrhenius equation.

Paper kinetic parameters and approximate service life are shown in Table I.

Table I

No	Kind of paper	Kind of polymer	U_0 , J/mol	U , J/mol	Service life, years
1	100% sulfate cellulose	-	136200 (28800)*	92600 (18900)	80
2	- " -	Polyvinylalcohol 3,5% solution put on the surface	146000 (29800)	99500 (20300)	900
3	100% cotton	-	129400 (26400)	92600 (18900)	100
4	- " -	Polyvinylalcohol 3,5% solution put on the surface	141100 (28800)	98500 (20100)	800
5	- " -	NaCMC, 3,5% solution put on the surface	141600 (28900)	99500 (20300)	1100
6	Newspaper	-	115600 (23600)	91100 (18600)	25
7	- " -	Polyethylene film, impregnation	129400 (26400)	97500 (19900)	200

As seen from the table, the given activation energies of the destruction process of the paper which is not under the load are similar to those obtained by many authors for thermodestruction of paper (24-30 kkal/mol). As to the calculated values of lifetime they correspond to the known periods of paper service life.

The described method of evaluating durability may be used for an estimation of any influence on paper in the process of restoration, for instance, bleaching, cleaning, processing with ferments or antiseptics.

* The values given in brackets are expressed in kkal/mol.

Thus, it is suggested that new method of evaluation of paper lifetime with the use of thermofluctuation concept of strength should be used for which it is sufficient to determine the folding endurance and stiffness during bending. The method allows to evaluate the relative influence of polymeric additives on paper durability escaping artificial heat aging. The whole process of measuring and calculating is simple, does not require any complicated equipment. It takes only from 7 to 8 hours to predict the service time of a paper.

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THE REGENERATION OF COLOUR OF THE
DARKENED LEAD WHITE BY METHOD OF
ABSORPTION OF HYDROGEN PEROXIDE
VAPOURS

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Zagreb, 1978

THE REGENERATION OF COLOUR OF THE DARKENED LEAD WHITE BY
METHOD OF ABSORPTION OF HYDROGEN PEROXIDE VAPOURS

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The report deals with a problem of regeneration of colour of the darkened lead white. It is based on the numerous experimental and practical works performed in the field of restoration of european and oriental drawings at the Russian Art Restoration Centre I.E.Grabar from 1953 to 1977. There are concrete recommendations and recipes in the report.

Darkening of lead white is often a case in guache and water-colour works, where lead white is not enough defended by a binder. The colour is usually regenerated by the hydrogen peroxide. In special literature there are well-described methods which we think is necessary to examine in this report.

An English scientist A.Scott points out in his method that because of the presence of toxic impurities in hydrogen peroxide, such as sulphuric acid, phosphoric acid and salts - it is necessary to use for a practical work a plate of 'Paris' gypsum as an active surface producing vapours of hydrogen peroxide.

A drawing is put face down on this plate at a distance of 1/8" for several hours. But even at a considerable distance from a plate the middle part of a drawing swells more than the edges, it wrinkles and other defor-

mations appear which are difficult to eliminate even under a heavy press. Besides this method destroys the paper.

Scott proposes 3 methods of application of hydrogen peroxide:

- 1) Hydrogen peroxide concentrated on a gypsum plate;
- 2) Hydrogen peroxide concentrated in a sulphuric ether;
- 3) Hydrogen peroxide concentrated and mixed with equal part of alcohol.

The second and third methods suppose that the solutions should be put on darkened areas with a soft brush.

A well-known English restorer Plenderleith improved Scott's method. He proposed to put on the drawing brush parallel strips of ether solution of Hydrogen peroxide. To accelerate the process the author recommends to add a drop of perhydrol and to subject a drawing to the concentrated ammonia vapours. So the process of regeneration goes on without wetting. The author proposes also the tamping by ether solution of Hydrogen peroxide. It is possible to prolong its action by adding a drop of perhydrol to ether and by putting ether solution with a brush on the darkened lead white.

So all the proposed methods provide the regeneration of the colour of darkened lead white with hydrogen peroxide:

- 1) by keeping the drawing for several hours over hydrogen peroxide vapours;
- 2) by brushing the solutions directly to the darkened areas.

The application of the above-

mentioned methods requires a great attention as the occasional spilling of the solution during the brushing is undesirable and often non permissible. The prolonged keeping over the vapours of hydrogen peroxide as well as long brushing have a destructive effect upon the paper and the paint layer.

A suggested method of regeneration of lead white is equally applicable for the drawings in water-colour and gouache on various types of paper and different state of conservation of paper and paint-layer. The basis of our method is the recipe of Plenderleith (ether solution of perhydrol combined with vapours of ammonia concentrated). But our method is not a result of a mechanical transfer of the Plenderleith's method on concrete objects, it has a number of important peculiarities. Here is the detailed description of the method, materials and instruments:

1. Two equal capacities 1 and 11 with flat bottoms, 2-3 cm high are required. We used box covers with diameter 5 cm. On the bottom of the inner side of each cover we attach with a glue a circle of felt or technical tarpaulia of the same diameter.

2. Small windows are cut in a sheet of thick paper corresponding to the parts of a drawing with darkened lead white. Dimensions of these windows must be 0,5 cm smaller in radius than those of a cover.

3. In a measuring-cylinder with a ground-in stopper we put 1 volume of perhydrol and 2 volumes of sulphuric

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ether. The mixture is to be shaken just before it is put to a felt circle.

4. With a glass stick we put to the felt of the cover 1 2-3 drops from the ether layer saturated with perhydrol; immediately after that the cover is turned upside-down on the sheet of thick paper.

5. To the felt of the cover 11 we put with the same stick 2-3 drops of the solution of ammonia concentrated. Then the cover is turned upside-down beside the cover 1.

6. With a sliding movement we move the cover 1 along the paper keeping it for 1-2 minutes over the parts with darkened lead white.

7. After 1-2 minutes the cover 1 is substituted by the cover 11 with the same sliding movement. The ammonia vapours regenerate the colour more intensively. By alternative action of the ammonia vapours and hydrogen peroxide the colour of lead white is regenerated.

8. Then the drawing is left open for two weeks; the paper acidity should achieve pH 6,0 - 7,0.

9. The drawing is washed on filter paper with distilled water.

In 1953 we restored by this method the colour of darkened lead white on a water-colour drawing of a Russian painter F.M. Matveev (1798-1826) 'An Italian Landscape' (16,0 X 23,0 cm); it was sent to us for restoration from the State Tretjakov Gallery.

Good results were achieved in 1967 during the resto-

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ration of a drawing of an unknown painter of the Italian school of the XVI-th century - 'The Saint Family'; the technique of the drawing - pen, bistre, white. All the high lights painted in white turned out into black spots. The base of the drawing - European manufactured paper with a superficial sizing. A very thin layer of lead white was put by a painter over a paint layer (and over the thick sizing of a paper), that's why the regeneration had gone easily and quickly. Lead white was identified by nitrous acid test and by reaction with benzidine.

We restored many drawings of occidental school from the museums of our country with the regeneration of lead white and now after 10-15 years they are in a good state. We think it is necessary to outline the peculiarities of the application of this method for the restoration of oriental painting - Chinese rolls of the beginning of the XIX-th century. It is known that the Chinese rolls are done on the finest rice paper, weakly sized, glued with a gum in 4-5 layers.

A thin layer of lead white is put on a paper under the most important parts of painting (face, hands). Besides lead white was used for high lights.

In this case we see a complicated combination of dilapidated base, large area of darkened white and white that had been under the painting and passed to the reverse side.

Having considered all these difficulties we continued

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our work with the experimental material. As a result we elaborated the method described below, based on the moistening and acidifying with vapours of hydrochloric acid. (Preparatory work was similar to the processes mentioned above, see pp.1-5).

The areas of darkened white passed to the reverse side were acidified in the following way. On the bottom of a laboratory cuvette 5 x 5 cm we put a sheet of filter paper wetting it with a drip of concentrated hydrochloric acid. Then the cuvette was put for several seconds under the treated areas. The alternative use of vapours of perhydrol with ether and of ammonia during 1,5 - 2 hours brought to complete regeneration of the colour of lead white. For the regeneration of darkened lead white in high lights it is enough to moisten the area with distilled water (the water is wringed out with a roller from a moderately moistened filter paper sheet, cut out according to the dimensions of a damaged area) and then to treat them with vapours of acidifier and ammonia. After the chemical treatment the rolls were washed on filter paper, moistened with distilled water.

This method has been tested for more than 25 years; it is widely used for different basis and different techniques; it doesn't effect negatively materials and paintings, because the reactions effect only the areas of darkened lead white and during the process of absorption of reagents' vapours by the paper. The repeated darkening

of lead white was not observed in any drawing.

The first drawing of F.M. Matveev with restored lead white was exhibited in 1967 at the Sixth Exhibition of the Russian Art Restoration Centre and later it was shown at the Exhibition 'Chemistry-70' in 1970 and in Bulgaria in 1974. The Chinese rolls are exhibited in various museums of our country.

All above-said permits us to recommend the method for the restoration of works of art on paper. The methods were described in the book 'The Problems of Restoration and Conservation of Works of Fine Art' (Publishing House, the USSR, Academy of Fine Arts, Moscow, 1960).

The report will be illustrated.

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EFFET DE LA LYOPHILISATION SUR LE
COMPORTEMENT MECANIQUE ET CHIMIQUE
DU PAPIER, DU CUIR ET DU PARCHEMIN

Françoise Flieder, Françoise Leclerc
et Claire Chahine

Comité pour la conservation de l'ICOM
5ème Réunion triennale
Zagreb, 1978

EFFET DE LA LYOPHILISATION SUR LE COMPORTEMENT MECANIQUE ET CHIMIQUE DU PAPIER, DU CUIR ET DU PARCHEMIN

Françoise Flieder, Françoise Leclerc et Claire Chahine

RESUME

Le séchage rapide de documents gorgés d'eau a toujours été un problème difficile à résoudre.

On a expérimenté avec succès depuis quelques années une nouvelle technique d'assèchement qui utilise l'action combinée du froid et du vide. Il s'agit de la *lyophilisation*. Ce procédé rapide évite la prolifération des microorganismes, ainsi que la solubilisation tant de l'encre que de la couche picturale des enluminures.

Nous avons voulu vérifier expérimentalement que les constantes mécaniques et chimiques des constituants des documents graphiques n'étaient pas modifiées par la lyophilisation. Dans ce but, des papiers, des cuirs et des parchemins ont été traités par deux techniques différentes de lyophilisation. Si les résultats sont très satisfaisants en ce qui concerne les papiers et les cuirs, la résistance mécanique du parchemin est par contre modifiée, car la lyophilisation provoque un épaissement et donc, une diminution d'élasticité de ce matériau. Ce phénomène est néanmoins réversible.

La congélation peut toutefois être utilisée comme méthode de stockage de tous ces matériaux, y compris le parchemin.

L'eau entraîne souvent des méfaits considérables sur les documents graphiques. L'origine de ces sinistres peut être soit naturelle (crues de fleuves ou rivières, orages, tempêtes ...), soit accidentelle (rupture de canalisations, fuite de toiture, murs lézardés, eau utilisée lors d'incendies ...). En quelques minutes, des dizaines de milliers de livres, manuscrits et liasses d'archives peuvent être ainsi inondés. Le problème de leur sauvetage est une préoccupation essentielle pour tous les responsables de collections. Cette tâche est difficile, car il faut agir très vite et sur une masse très importante de documents.

On se souvient de l'ampleur des dégâts causés par certains sinistres tels que les inondations de Florence et de Venise en 1966 (1), le débordement du Tage à Lisbonne qui, en 1967, submergea la totalité des oeuvres d'art de la collection Calouste Gulbenkian ; enfin les méfaits du fameux ouragan "Celia" qui dévasta au Texas en 1970, 50.000 livres conservés à la Bibliothèque universitaire de Corpus Christi (2). A cette époque-là, les moyens rapides d'assèchement n'étaient pas encore connus. On utilisait donc des procédés classiques : interfoliage (placer entre chaque page d'un livre une ou deux feuilles de papier buvard), aspersion de talc, radiations infra-rouges, ventilation d'air chaud, etc ... Ces techniques étaient toutes très contestables et très lentes. Les documents qui restaient ainsi gorgés d'eau pendant des semaines, voire même pendant des

mois, se détérioraient rapidement. L'encre des manuscrits très souvent soluble à l'eau disparaissait et la couche picturale des enluminures ruisselait le long du parchemin entraînant un mélange de liants et de pigments. De plus, cet excès d'humidité favorisait la croissance de microorganismes et de nombreuses taches colorées apparaissaient ainsi en quelques jours sur les supports.

Afin d'éviter de telles catastrophes, il fallut trouver une méthode d'assèchement très rapide. Les Danois pensèrent les premiers à utiliser la congélation. A ces très basses températures, aucun développement de microorganismes ne pouvait se produire et la solubilisation des encres et des peintures était immédiatement stoppée. Des milliers de documents de la collection Kleinschmidt qui avaient été inondés lors de l'extinction de l'incendie de la Greenland Regional Library dans le Godthåb durant l'hiver 1968 furent ainsi congelés (3). Tous ces livres et manuscrits sont restés dans les installations industrielles pendant deux ans jusqu'à ce qu'une décision soit prise pour le choix de la technique d'assèchement à employer. Au mois d'août 1972, des milliers de livres inondés dans les caves de la bibliothèque de Stuttgart furent également congelés (4) (5).

Le premier stade du traitement était trouvé ; les documents ainsi stabilisés pouvaient attendre des années que leur restauration soit effectuée. Peter WATERS (6) signale même que certains manuscrits sont restés plus de 6 ans dans des congélateurs maintenus à -20° , sans aucun dommage. Ce système présentait néanmoins l'inconvénient de bloquer pendant de très longues périodes des installations frigorifiques. Pour résoudre cette difficulté, on essaya d'utiliser pour assécher les documents congelés une technique couramment employée dans l'industrie alimentaire pour déshydrater les végétaux : la lyophilisation (7).

C'est un procédé qui utilise l'action combinée du froid et du vide : l'eau est transformée en glace, puis sublimée par conversion directe de la phase solide à la phase gazeuse, sans jamais passer par la phase liquide. L'appareil à lyophiliser comprend une cuve de congélation, un condensateur qui piège les molécules d'eau et une pompe à vide permettant d'abaisser la pression à l'intérieur de l'appareil à environ 10 mm de mercure.

A notre connaissance, deux fonds de bibliothèques inondés ont été traités expérimentalement de la sorte. Le premier traitement a été réalisé au Danemark au *Food Technology Laboratory* à Lyngby sur les livres provenant de la Greenland Regional Library deux ans après l'incendie. Les résultats obtenus furent excellents. Le deuxième traitement a été effectué aux U.S.A. par la General Electric's Company sur les 60.000 documents de la bibliothèque de la *Temple University's Klein Law* de Philadelphie (8) (9) qui avaient été gorgés d'eau lors d'un incendie en 1972. Après avoir été congelés à -30° par les soins de la Library of Congress, les livres ont été envoyés au Valley Forge Space Center où ils furent lyophilisés dans une des enceintes à vide destinées à tester les satellites. L'opération qui dura une année donna des résultats très satisfaisants.

La lyophilisation nous semblant donc une solution d'avenir pour les traitements de masse, avant de l'utiliser à grande échelle, il nous a paru indispensable de s'assurer que les documents graphiques ne risquaient pas d'être endommagés par un tel traitement. Dans ce but, nous avons étudié la résistance mécanique et chimique des papiers, cuirs et parchemins lyophilisés.

1. PROTOCOLE D'ESSAI

Tous les échantillons avant d'être lyophilisés ont été immergés pendant un temps qui a varié en fonction de leur pouvoir d'absorption de l'eau. Deux techniques de lyophilisation ont été employées.

- *traitement 1*, réalisé au Museum national d'Histoire naturelle*, dans une petite enceinte expérimentale S.E.R.A.L. (réf. RP 45). Les échantillons ont été congelés pendant 5 heures à -35° , puis lyophilisés sous un vide de 3×10^{-1} mm de mercure à -20° pendant un temps qui a varié de 3 à 4 jours, en fonction de l'épaisseur des matériaux. La température a été ensuite remontée à $+15^{\circ}$ en quelques heures et maintenue à ce niveau pendant 24 à 48 heures sans ouvrir l'appareil. On s'assure ainsi de conserver une humidité résiduelle aux échantillons.

- *traitement 2*, effectué dans un sublimateur de laboratoire (type S.M.J.B.) de la Société USIFROID. Les échantillons ont été congelés pendant 3 heures à -40° , puis la sublimation de l'eau a été réalisée sous un vide de 5×10^{-1} mm de mercure à -20° pendant un temps qui a varié entre 24 heures et 3 jours. Le vide a été rompu en quelques minutes et la température des échantillons est ramenée à celle des étagères, aux environs de 30° ; ils séjournent dans l'appareil encore une dizaine d'heures.

Nous tenons à remercier ici toutes les personnes qui ont aimablement collaboré à cette étude :

Les techniciennes du Centre de Recherches sur la Conservation des Documents Graphiques ;

Mlle MEURGUES, Maître-assistant au Laboratoire de Naturalisation au Museum national d'Histoire naturelle ;

Mme JANNIERE, Assistante au Laboratoire de Naturalisation ;

M. LARRAT de la Société USIFROID.

2. COMPORTEMENT DES PAPIERS LYOPHILISES

L'expérimentation a été menée sur deux sortes de papiers :

- un papier AFNOR VII/5 (100 % pâte de linters de coton)
- un papier AFNOR VII/1 (100 % pâte chimique blanchie)

Les mesures de résistances mécaniques et chimiques, ainsi que les variations des constantes optiques ont été effectuées suivant les normes AFNOR et TAPPI* :

résistance à la traction, au pliage, à l'éclatement, au déchirement, pour les tests mécaniques ;

mesures de pH, du degré d'oxydation et de polymérisation de la cellulose, pour les tests chimiques ;

mesures de blancheur et d'opacité, pour les tests optiques.

Nous avons étudié comparativement la résistance mécanique et chimique du papier témoin (avant immersion), du papier immergé et séché à l'air et du papier immergé et lyophilisé. Afin de connaître le comportement dans le temps des échantillons ainsi traités, nous les avons soumis à un cycle de vieillissement accéléré (3 jours en étuve sèche ventilée maintenue à 105°C).

L'eau solubilisant certains produits de dégradation provenant de l'oxydation de la cellulose, les papiers immergés dans une eau pure présentent de ce fait une légère amélioration de leurs constantes. Les papiers mouillés et séchés à l'air ont donc une résistance légèrement supérieure à celle du témoin, c'est pourquoi nous avons décidé de comparer les papiers lyophilisés aux papiers témoins (tableaux traitement 1 et traitement 2)**.

La surface du papier Afnor VII/1 après lyophilisation est partiellement recouverte par une fine poudre blanche qui lui donne un aspect légèrement brillant. L'analyse de celle-ci par spectroscopie infra-rouge et microscopie nous a montré qu'il s'agissait d'amidon. Cet amidon provient d'un liant entrant dans la composition de certains papiers d'édition. Néanmoins, ce dépôt peut être éliminé facilement par broissage et, comme nous pouvons le constater d'après les tableaux, la résistance mécanique et chimique de ce papier a été peu modifiée par la lyophilisation, à l'exception d'une faible diminution de la résistance à la traction (traitement 1), ainsi qu'une légère augmentation de l'indice de cuivre (traitement 2).

Le papier Afnor VII/5 a également bien réagi ; nous notons, cependant, une faible diminution de la résistance au pliage (traitement 1) et de l'indice de cuivre (traitement 2).

Dans ces conditions, nous pensons que la lyophilisation est une méthode tout indiquée pour l'assèchement des papiers.

* AFNOR, NFQ 03.001, 03.011, 03.004, 03.014, NFT 12.002, 12.004, 12.005
TAPPI, T 435 m 52

** Les essais de résistances mécaniques sont effectués en atmosphère conditionnée, pour le tableau 1 à 21°C, 65 % H.R. et pour le tableau 2 à 23°C, 50 % H.R., la normalisation de ce conditionnement ayant changé entre les deux séries d'essais.

3. COMPORTEMENT DU CUIR ET DU PARCHEMIN LYOPHILISÉS

Nous avons réalisé notre étude sur du cuir de veau et du parchemin de mouton. Les échantillons ont été découpés suivant la technique habituelle des carrés latins (10). Nous avons étudié comparativement des échantillons séchés naturellement à l'air, et des échantillons soumis à la lyophilisation (traitement 2).

La première constatation est visuelle :

- les parchemins ayant séché à l'air se sont déformés et raccornis, ce qui est logique, puisqu'ils n'ont pas été étirés au cours du séchage. Les parchemins lyophilisés ont un aspect tout à fait surprenant : ils ont considérablement épaissi (presque du double), durci et de plus leur couleur s'est éclaircie. La rétraction est assez importante dans les deux cas : 4 à 5 % pour ceux séchés à l'air, 5 à 6 % pour ceux lyophilisés.
- Les cuirs lyophilisés ont eux aussi légèrement pâli et leurs dimensions se sont modifiées : le retrait est de 4 % environ, contre moins de 1 % pour les échantillons séchés à l'air. Néanmoins, on ne constate pas d'épaississement après lyophilisation.

Des tests mécaniques analogues à ceux du papier ont été réalisés selon les normes Afnor* sur ces échantillons de cuir et de parchemin : résistance à la traction et allongement à la rupture, à l'éclatement, au déchirement (signalons que le parchemin ne peut être soumis à ce test car il se dédouble). Nous avons également effectué des tests chimiques : taux d'humidité et de matières grasses, pH et indice de différence, dosage de l'azote dans l'extrait aqueux (10).

D'après le tableau (traitement 2), on constate que le cuir lyophilisé ne subit que de très faibles modifications de ses propriétés mécaniques et pas de modification de ses propriétés chimiques, si ce n'est une perte d'humidité.

Nous pensons donc que la lyophilisation peut être utilisée sans grand risque pour le séchage du cuir.

Le parchemin n'a pas réagi de la même façon (tableau traitement 2-parchemin 1) : on observe une perte très importante de la résistance mécanique (de l'ordre de 50 %). Les propriétés chimiques sont peu modifiées, à l'exception là aussi du taux d'humidité. Devant une telle détérioration physique du parchemin, nous avons décidé de répéter nos expériences mais en faisant cette fois lyophiliser nos échantillons dans l'appareil du Museum national d'Histoire naturelle (traitement 1) qui utilise une technique de réchauffement moins brutale. Des résultats identiques ont été obtenus (voir tableau traitement 1-parchemin 2).

* Normes Afnor NFG 52.002, NFQ 03.001, NFG 52.014, NFG 42.202, NFG 52.204, NFG 52.214.

Il nous a paru intéressant de connaître à quel niveau se situait la détérioration : congélation ou lyophilisation ? Des échantillons de parchemin ont été soumis à -35° pendant plusieurs heures. Par examen visuel, on constate uniquement la déformation due à l'absence d'étirement au cours du séchage, il n'y a aucun épaississement, ni changement de couleur.

D'autre part, nous avons voulu vérifier si la détérioration du parchemin provoquée par la lyophilisation était réversible. Nous avons donc fait restaurer nos parchemins lyophilisés par l'atelier de restauration de la Bibliothèque nationale : ils ont été remouillés, puis mis à sécher sous presse pendant quelques jours. Nous avons alors constaté qu'ils reprenaient leur aspect original : souplesse, couleur, épaisseur étaient redevenues normales.

Afin de vérifier toutes ces constatations visuelles, nous avons comparé la résistance mécanique du parchemin séché sous presse à celle du parchemin lyophilisé et restauré et à celle du parchemin congelé-dégelé-séché sous presse.

Seuls les tests mécaniques ont été effectués, car nous avons observé précédemment que la lyophilisation modifiait très peu la résistance chimique du parchemin. D'après le tableau traitement 1-parchemin³, nous ne constatons aucune différence appréciable des propriétés mécaniques de ces trois parchemins.

Il apparaît ainsi qu'un parchemin lyophilisé subit une détérioration importante mais réversible et qu'un parchemin inondé peut supporter sans dommage la congélation à condition toutefois qu'il soit mis sous presse pendant le séchage dès que sa température est remontée au-dessus de 0° .

4. CONCLUSION

De l'ensemble de ces résultats, il ressort que la lyophilisation devrait prendre dans les années qui viennent un très grand essor pour le séchage rapide des livres gorgés d'eau.

Ce procédé a l'avantage de pouvoir traiter en une seule opération un grand nombre de documents. Si le papier et le cuir réagissent bien, il n'en est pas de même pour le parchemin qui nécessite quelques précautions pour le séchage. Il est donc recommandé, en cas de sinistre, de retirer systématiquement tous les manuscrits sur parchemin et de les entreposer dans des congélateurs le temps nécessaire à leur restauration.

La lyophilisation exige néanmoins des installations importantes et onéreuses qui ne sont pas toujours mises à la disposition des conservateurs. Dans ce cas, il est important de procéder rapidement à une congélation des documents dans des installations industrielles ou même domestiques. Ceux-ci peuvent rester ainsi stabilisés pendant plusieurs années dans l'attente d'un traitement.

* Ce travail a été réalisé grâce à la coopération de Mme PETIT, Chef de l'atelier de restauration de la Bibliothèque nationale, que nous remercions ici.

La lyophilisation n'est cependant pas l'unique procédé d'assèchement rapide, d'autres techniques telles que les micro-ondes sont en expérimentation actuellement (11)

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RESISTANCE MECANIQUE ET CHIMIQUE DE DEUX PAPIERS LYOPHILISES
(traitement 1)

78/14/8/8

	Afnor VII/5			Afnor VII/1		
	Témoïn	Traité	Vieilli	Témoïn	Traité	Vieilli
			traite			traite
Longueur de rupture en m.						
ST	2080	1975	1945	1790	3295	3610
SM	3210	3265	3185	3000	5740	6635
Résistance au pliage						
ST	147	121	50	56	136	102
SM	561	481	188	194	452	201
Résistance à l'éclatement						
ST	2,10	2,13	1,83	1,81	3,22	2,85
SM	1222	1326	1005	1096	1144	968
Résistance au déchirement						
ST	1024	1037	760	1020	1273	1020
SM	860	822	630	650	724	630
D.P.v.						
Indice de cuivre						
ST	0,40	0,33	0,89	0,60	0,75	1,45
SM	6,30	5,60	5,80	5,65	6,15	5,60
pH						
ST	80	80	76,5	76,5	84	72
SM	93	93	93,5	93,5	89	86
Blancheur						
ST						
SM						
Opacité						
ST						
SM						

RESISTANCE MECANIQUE ET CHIMIQUE DE DEUX PAPIERS LYOPHILISES
(traitement 2)

78/14/8/9

	Afnor VII/5				Afnor VII/1			
	Témoin	Traité	Vieilli	Vieilli traité	Témoin	Traité	Vieilli	Vieilli traité
Longueur de rupture en m.								
ST	2245	2135	2070	2030	3995	3925	3810	3845
SM	3655	3530	3590	3535	7805	7325	7660	7370
Résistance								
ST	131	117	50	55	160	180	82	98
SM	435	616	143	180	266	274	130	172
Résistance à l'éclatement								
	2,00	2,06	1,80	1,86	3,32	3,50	3,16	3,19
Résistance au déchirement								
ST	1102	1197	967	1011	1119	1130	952	1027
SM	918	972	785	847	1118	1050	899	1012
D.P.v	860	798	630	594	730	733	630	627
Indice de cuivre								
	0,40	0,45	0,89	0,81	0,71	0,85	1,45	1,39
pH								
	5,80	5,70	5,80	6,10	5,90	6,35	5,60	6,35
Blancheur								
	77,3	77,5	73,5	75,0	80,1	81,1	70,7	70,7
Opacité								
	97,8	97,6	98,4	98,7	92,6	93,3	96,8	97,5

RESISTANCE MECANIQUE ET CHIMIQUE DU CUIR ET DU PARCHEMIN LYOPHILISES (traitement 2)

78/14/8/10

	C U I R		PARCHEMIN (1)	
	séché à l'air	lyophilisé	séché à l'air	lyophilisé
Résistance à la traction da N/mm ²				
ST	1,54	1,75	4,54	3,08
SE	1,92	1,94	7,64	4,21
Allongement à la rupture %				
ST	32,8	33,3	19,9	16,8
SE	33	35,1	16,5	16,4
Résistance à l'éclatement kg/mm				
ST	28,3	28,3	79,9	41,8
Résistance au déchirement da N/mm				
ST	3,12	2,78		
SE	3,02	2,76		
Matières volatiles %				
	11,2	10,2	14,6	13,4
Matières grasses %				
	1,7	1,7	0,6	0,6
pH				
dilution au 1/10e	5,35	5,05	8,25	8,25
indice de différence	5,70	5,50	7,65	7,65
	0,35	0,45	0,60	0,60
Azote soluble %				
	0,04	0,04	0,28	0,51

RESISTANCE MECANIQUE ET CHIMIQUE DU PARCHEMIN LYOPHILISE
(traitement 1)

	PARCHEMIN (2)		PARCHEMIN (3)		
	séch� à l'air	lyophilisé	séch� sous presse	lyophilisé restaur�	congel� s�ch� sous presse
Resistance � la traction da N/mm ²					
ST	4,21	2,77	5,02	4,81	4,83
SE	6,27	3,74	6,42	6,62	
Allongement � la rupture %					
ST	21	19,1	12,5	11,4	13,1
SE	18,8	19,2	12,9	13,4	
Resistance � l'�clatement kg/mm					
	66,6	35,7	67,2	62,3	64,9
Resistance au d�chirement					
ST					
SE					
da l/mm					
Mati�res volatiles %	12	11,1			
Mati�res grasses %	1,1	1,1			
pH	7,65	7,70			
dilution au 1/10e	6,85	6,85			
indice de diff�rence	0,80	0,85			
Azote soluble %	0,11	0,12			

78/14/8/11

78/14/9

ETUDE DE LA REGENERATION CHIMIQUE
DES ENCREs METALLO-GALLIQUES

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ETUDE DE LA REGENERATION CHIMIQUE DES ENCREs METALLO-GALLIQUES

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RESUME

Les encres métallogalliques sont sujettes à certaines détériorations. Un ensemble de facteurs qui dépend à la fois de leur fabrication, de leur utilisation ainsi que du milieu dans lequel elles ont été conservées peut entraîner leur pâlissement. De nombreux auteurs se sont penchés depuis longtemps sur ce phénomène et ont essayé d'y remédier par des méthodes chimiques. Nous en avons expérimenté un grand nombre et avons mis au point d'autres procédés en tenant compte de leur efficacité et de leur innocuité vis-à-vis du support.

Les essais ont été menés, d'une part sur des échantillons manuscrits, d'autre part sur des papiers modernes. Afin de vérifier le comportement de la régénération dans le temps, les échantillons ont été soumis à plusieurs sortes de vieillissement artificiel. La résistance mécanico-chimique a été examinée sur les documents traités avant et après ce vieillissement. Nous avons ainsi pu retenir plusieurs méthodes de révélation utilisant, soit l'acide gallique, soit l'8-hydroxyquinoléine, soit le sulfure d'ammonium, cette dernière ayant l'inconvénient d'être d'un emploi plus délicat.

INTRODUCTION

Il existe deux grandes catégories d'encres noires : les encres au carbone et les encres métallogalliques.

Les encres au carbone sont essentiellement constituées de noir de fumée obtenu à partir de la combustion de substances végétales ou animales dont les particules sont maintenues en suspension par un liant. *Les encres métallogalliques* sont une combinaison de matières tanniques, de sels métalliques, d'un liant, d'un solvant et d'adjuvants divers. Il se forme alors, entre les substances tannantes et les sels métalliques un complexe qui, en présence de l'oxygène atmosphérique, se transforme en gallo-tannate métallique d'une couleur noire intense. La fabrication de ces encres a évolué dans le temps et particulièrement au siècle dernier.

Les encres au carbone sont généralement indélébiles, alors que les encres métallogalliques se détériorent, soit en corrodant leur support par un excès d'acidité, soit en pâlisant. C'est de ce second phénomène dont il sera question ici.

Dans certains cas, la couleur noire d'origine est passée du brun rouille au jaune ; elle a parfois pâli au point de rendre le texte illisible.

Ce phénomène est souvent dû à une transformation des acides carboxyphénoliques, les produits de décomposition de ces acides ne pouvant pas se complexer avec les traces d'oxyde métallique restant sur le support.

De nombreux facteurs sont à l'origine de ce pâlissement :

- *les facteurs externes* : effets de l'environnement (oxygène, humidité, lumière, pollution)
- *les facteurs internes* :
 - . nature, qualité, proportions des constituants
 - . nature des supports
 - . nature de l'instrument qui conditionne un dépôt plus ou moins important d'encre sur le support.

Deux procédés différents offrent la possibilité de faire réapparaître les écrits pâlis :

- la première méthode ne nécessite aucune intervention sur le manuscrit lui-même et permet de déchiffrer le texte, soit momentanément par une exposition à des rayons U.V. ou I.R., soit définitivement à l'aide d'une photographie du document avec amplification du contraste.
- la deuxième méthode consiste à traiter le document par diverses solutions afin de redonner à l'écriture une certaine coloration, la plus proche possible de celle d'origine.

Ce problème, qui a préoccupé de nombreux auteurs, a permis la mise au point d'un certain nombre de recettes que l'on classera ainsi :

- traitements à la noix de galle
- traitements au sulfure d'ammonium
- traitements au ferrocyanure de potassium
- traitements divers (8-hydroxyquinoléine, nitrate d'argent)

PROTOCOLE D'ANALYSE

Parmi les nombreuses méthodes décrites dans la littérature, nous avons d'abord éliminé les traitements qui nous paraissaient soit néfastes pour le support, soit inacceptables pour la coloration obtenue.

Nous avons expérimenté toutes les autres méthodes en étudiant l'efficacité de la révélation et les modifications tant de la coloration du support que de son acidité.

Certaines techniques ont été retenues, d'autres, très modifiées aussi bien du point de vue de la concentration des produits que du mode opératoire.

De plus, le choix d'une méthode appropriée doit tenir compte d'une part de la sensibilité de certaines encres métallo-galliques à l'eau et aux solvants organiques, (ce qui nécessitera avant tout traitement d'effectuer des tests afin d'utiliser le solvant le mieux approprié); d'autre part de la présence dans le support de traces métalliques (fer), provenant de poussières ou de manipulations. Celles-ci réagissent aux traitements chimiques au même titre que l'écrit et peuvent entraîner une coloration du support. Afin d'éliminer au maximum, l'effet néfaste de ces éléments, tous les papiers devront être nettoyés avant chaque traitement.

Nous avons étudié l'efficacité des différents procédés de révélation sur des échantillons manuscrits datant du XVII^e et du XVIII^e siècles dont l'encre ferro-gallique était soluble à l'eau. Afin d'estimer la stabilité du traitement dans le temps, les échantillons régénérés ont été exposés pendant 96 heures à des radiations émises par une lampe au xénon*. Nous avons ensuite examiné le comportement des papiers traités par les méthodes ainsi sélectionnées. L'expérimentation a été menée sur deux papiers de composition différente :

pâte 100 % pur chiffon (Afnor VII/5)

pâte 100 % chimique blanchie (Afnor VII/1)

Les essais ont été effectués selon les normes Afnor et Tappi avant et après vieillissement artificiel (72 heures dans une étuve sèche, ventilée maintenue à 105°C).

Une première sélection rapide a été faite à partir des résultats de blancheur et d'acidité**. L'ensemble des papiers traités a été entreposé pendant plusieurs semaines dans une salle climatisée (23°C - 50 % H.R.), afin d'observer une éventuelle évolution de leur coloration dans le temps.

Nous avons ensuite vérifié la résistance mécanique et chimique de ces papiers (résistance à la pliure, à la rupture, à l'éclatement, à la déchirure, degré de polymérisation, indice de cuivre***).

EXPERIMENTATION

Seules les méthodes de révélation à base d'acide gallique, de 8-hydroxyquinoléine et de sulfure d'ammonium nous ont paru intéressantes. Nous nous sommes efforcées d'étudier de manière exhaustive chacun de ces trois procédés.

1. Régénération à l'acide gallique

Après avoir entrepris de nombreux essais sur les méthodes décrites dans la littérature utilisant diverses substances tannantes, notre choix s'est fixé sur l'acide gallique pur.

Les solutions aqueuses offrent l'avantage d'une bonne régénération mais font diffuser l'encre autour des caractères. Les solutions alcooliques ne présentent pas cet inconvénient, mais la révélation est moins intense. Nous avons donc adopté un mélange eau-alcool en ayant soin d'utiliser une quantité d'alcool suffisante pour éviter la solubilisation de l'encre.

* Lampe de 1500 watts dans un Xénotest maintenu à 25°C et 60 % H.R.

** Afnor NFQ 03.006, NFQ 03.008 et TAPPI T 435 m 52.

*** NFQ 03.004, NFQ 03.001, NFQ 03.053, NFQ 03.011, NFT 12.005, NFT 12.004.

Afin d'éliminer au maximum l'acide gallique restant dans le papier après la régénération, nous avons effectué un rinçage à l'alcool. Le temps idéal de rinçage a été fixé à 28 heures avec renouvellements du bain.

Un traitement supplémentaire au bicarbonate de calcium a permis d'améliorer les blancheurs et d'augmenter légèrement les pH (cf. tableau n° 1).

Nous avons ainsi progressivement mis au point la technique suivante :

0,8 g. d'acide gallique sont dissous dans 100 ml d'une solution alcoolique diluée (90 ml d'alcool éthylique à 95° + 10 ml d'eau distillée). Les échantillons trempés pendant 5 minutes dans cette solution, sont ensuite séchés, rincés 28 heures dans de l'alcool éthylique, puis trempés 40 minutes dans une solution alcoolique à 2 % de bicarbonate de calcium.

L'encre des manuscrits ainsi traités s'est colorée en brun gris. Après exposition au rayonnement de la lampe au xénon, la coloration s'est légèrement atténuée.

La résistance mécanique des papiers traités n'est pas affectée, nous retenons même un accroissement de la résistance à la pliure (cf. tableau n° 1). Les constantes chimiques ne se trouvent pratiquement pas modifiées par ce traitement, à l'exception du degré d'oxydation de l'Afnor VII/5 avant vieillissement et de l'Afnor VII/1 après vieillissement qui a très notablement augmenté (cf. tableau n° 1).

Après vieillissement à la chaleur sèche, les papiers traités ont jauni. Nous avons remarqué que ce jaunissement n'avait pas évolué même après trois mois d'exposition dans une salle climatisée. Parallèlement, des papiers traités mais non vieillis ont été conservés dans cette salle : nous avons constaté une baisse sensible de leur degré de blancheur qui tend à se rapprocher des valeurs précédentes.

En conclusion, nous voyons que ce traitement entraîne une bonne régénération et qu'il ne semble pas altérer les constantes mécaniques et chimiques des papiers, en dehors d'une légère élévation du degré d'oxydation.

2. Régénération à la 8-hydroxyquinoléine

Comme point de départ à nos essais, nous avons appliqué la méthode de A. CHARRO-ARIAS (4) qui utilise une solution composée de 25 % de 8-hydroxyquinoléine et de 6 % d'acide acétique. L'eau a été remplacée par de l'alcool éthylique à 95°. Plusieurs concentrations ont été expérimentées allant de 1 à 10 %, limite de solubilité de la 8-hydroxyquinoléine. Nous avons ensuite fixé le temps de rinçage à 20 heures (avec renouvellement du bain) qui donne de très bons résultats pour les blancheurs et entraîne une légère augmentation des pH (cf. tableau n° 2). La technique que nous avons mise au point est la suivante :

les échantillons sont plongés pendant 5 minutes dans une solution alcoolique à 1 % de 8-hydroxyquinoléine et à 6 % d'acide acétique, puis séchés et rincés 20 heures dans de l'alcool.

Les encres ainsi régénérées acquièrent une coloration brun olive non modifiée après une irradiation de 96 heures.

Aucune modification des constantes mécaniques et chimiques n'a été remarquée (cf. tableau n° 2).

Après vieillissement à la chaleur sèche, le degré de blancheur des échantillons traités a diminué. Comme précédemment, une conservation de trois mois en salle climatisée a montré que ces valeurs s'étaient stabilisées alors que celles des papiers traités mais non vieillis continuaient à baisser. Il est important néanmoins de noter que les valeurs les plus basses restent nettement supérieures à celles que nous avons relevées sur les échantillons traités à l'acide gallique.

En conclusion, cette méthode donne de bons résultats. Une régénération à la 8-hydroxyquinoléine n'altère pas le papier. Elle semble même parfois augmenter sa résistance. La régénération est bonne mais peut-être moins conforme à l'idée que l'on se fait de l'original.

3. Régénération au sulfure d'ammonium

Nous nous sommes limitées dans ces essais à appliquer la méthode SANTUCCI (13) :

Ignier le document successivement dans :

- eau claire (5 minutes)
- solution de sulfure d'ammonium à 2 % (15 minutes)
- eau claire + 3 ml d'ammoniaque concentré/l (10-15 minutes)
- solution saturée d'acétate basique de plomb (5 minutes)
- solution d'acide acétique à 1 % (30 minutes)
- eau claire (20 minutes)

Les caractères sont régénérés en brun foncé d'une couleur très naturelle qui reste stable après passage dans le Xénotest.

Cependant, la méthode est longue car, comme le signale SANTUCCI, il est nécessaire de *changer la solution ammoniacale et la solution plombique pour chaque feuille ... d'avoir un grand volume de solution ammoniacale (5 litres par feuille). Le bain de plomb ... doit être également renouvelé dès qu'il commence à se troubler ou à noircir (13).*

De plus ce traitement malodorant doit être effectué sous des sorbonnes bien ventilées. En outre, c'est un traitement aqueux* qui risque dans certains cas de solubiliser les encres et d'entraîner une légère diffusion autour des caractères.

* Les solvants organiques n'étant pas compatibles avec certains produits chimiques utilisés, nous avons été obligés de conserver l'eau comme solvant.

78/14/9/6

L'expérimentation a été réalisée uniquement sur l'Afnor VII/1. Pour effectuer le traitement, nous avons maintenu le papier entre deux feuilles de mylar. Le mylar absorbant les solutions, la quantité de solution ammoniacale a dû être augmentée, le bain prolongé et changé.

Les constantes mécaniques et chimiques ne sont pas modifiées par ce traitement (cf. tableau n° 3).

Le vieillissement à la chaleur sèche a très légèrement jauni les papiers traités. Cette coloration s'est stabilisée après trois mois de conservation en salle climatisée. Contrairement aux deux autres procédés de régénération, le degré de blancheur des échantillons traités et non vieillis entreposés dans cette même salle a légèrement augmenté au bout d'un mois pour se stabiliser ensuite.

En conclusion, cette méthode nous paraît excellente tant du point de vue de la résistance mécanique et chimique que de la qualité et de la stabilité de la régénération. Cependant, il faudra toujours tenir compte de la nature des encres et du support qui réagissent différemment en fonction de leur composition. Par ailleurs, nous rappelons que ce traitement n'est pas d'une grande facilité d'exécution.

CONCLUSION

L'ensemble des travaux que nous venons de décrire nous a amené à sélectionner *trois méthodes* de révélation des encres métallogalliques pouvant s'appliquer *sans danger* et *donnant des résultats tout à fait satisfaisants*.

Néanmoins, nous tenons à signaler qu'il n'existe pas de méthode universelle et que ces traitements ne peuvent être utilisés sans discernement pour n'importe quel document, car il faut tenir compte à la fois de la nature des encres à traiter ainsi que de celle du support. En effet, l'intensité de la régénération dépendra avant tout de la quantité d'encre déposée à l'origine, ainsi que de la présence en plus ou en moins grande quantité d'oxyde métallique sur le support. Il faudra donc, avant tout traitement, effectuer une série d'essais, afin de s'assurer qu'il n'y a aucune incompatibilité entre la technique choisie et l'encre à révéler. Cet essai préliminaire sera réalisé avec le plus grand soin.

Nous tenons à remercier Mmes Martine LEROY et Sylvette BONNASSIES pour leur aimable collaboration.

LISTE DES PRINCIPAUX OUVRAGES REGROUPANT
des formules de révélation des encres

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T A B L E A U 1

RESISTANCE MECANICO-CHIMIQUE DE DEUX PAPIERS TRAITES A L'ACIDE GALLIQUE

	Longueur de rupture en mètres		Résistance à la pliure		Résist. à l'éclatém.	Résistance à la déchirure	Blan- cheur	D.P.v.	Indice de cuivre	pH
	ST	SM	ST	SM		ST	SM			
Afnor VII/5 témoin	2245	3655	131	435	2,00	1102	918	77,1	839	0,37 5,4
Afnor VII/5 traité	2312	3775	204	1011	2,30	1293	1029	74,7	781	0,60 5,3
Afnor VII/5 témoin vieilli	2070	3590	50	143	1,80	967	785	73,9	617	0,73 5,1
Afnor VII/5 traité vieilli	2145	3515	98	387	2,19	1138	994	67,2	627	0,80 5,6
Afnor VII/1 témoin	3335	6710	56	140	2,49	983	915	75,0	558	1,61 5,1
Afnor VII/1 traité	3880	6585	139	216	2,79	961	938	76,0	609	1,90 5,3
Afnor VII/1 témoin vieilli	3055	5920	14	15	2,05	737	713	62,3	450	1,66 4,9
Afnor VII/1 traité vieilli	3000	4820	40	29	2,31	765	719	64,6	492	2,13 5,3

Vieillissement : 72 heures à 105°C en étuve sèche ventilée

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RESISTANCE MECANICO-CHIMIQUE DE DEUX PAPIERS TRAITES A L'8-HYDROXYQUINOLEINE

	Longueur de		Résistance		Résist. à l'éclat.	Résistance		Blan- cheur	D.P.v.	Indice de cuivre	pH
	ST	SM	à la rupture en mètres	à la pluie		à la déchirure	ST				
Afnor VII/5 témoin	2245	3655		131	2,00	1102	918	77,1	839	0,37	5,4
	2270	3810		179	3,70	1211	1000	77,0	731	0,42	5,6
Afnor VII/5 traité	2070	3590		50	1,80	967	785	73,9	617	0,73	5,1
	2230	3710		87	3,47	1083	927	73,1	683	0,56	5,3
Afnor VII/1 témoin	3335	6710		56	2,49	983	915	75,0	558	1,61	5,1
	3125	6210		107	2,62	1043	900	76,9	614	1,49	5,5
Afnor VII/1 traité	3055	5920		14	2,05	737	713	62,3	450	1,66	4,9
	2975	6025		43	2,23	812	681	69,6	530	1,83	5,3

Vieillessement : 72 heures à 105°C en étuve sèche ventilée.

RESISTANCE MECANICO-CHIMIQUE DU PAPIER AFNOR VII/1 TRAITE AU SULFURE D'AMMONIUM

	Longueur de rupture en mètres		Résistance à la pliure		Résist. à l'éclat.	Résistance à la déchirure		Blanchéur	D.P.v.	Indice de cuivre	pH
	ST	SM	ST	SM		ST	SM				
Témoin	3335	6710	56	140	2,49	983	915	75,0	558	1,61	5,1
Traité	3061	6139	53	156	2,46	923	860	75,7	576	1,30	6,2
Témoin vieilli	3055	5920	14	15	2,05	737	713	62,3	450	1,89	4,9
Traité vieilli	2959	5713	29	45	2,33	775	689	68,3	494	1,53	6,0

78/14/9/11

Vieillissement : 72 heures à 105°C en étuve sèche ventilée



78/14/10

INVESTIGATION ON THE DISINFECTION BY
ETHYLENE OXIDE OF ILLUMINATED PARCHMENTS

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978

INVESTIGATION ON THE DISINFECTION BY ETHYLENE OXIDE OF ILLUMINATED PARCHMENTS

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Abstract

In order to employ ethylene oxide as disinfectant of illuminated books, we have carried out some checks based upon the measurement of viscosity and adhesion percentage of some adhesives used as a medium of pigments.

Furthermore, we have recorded the reflectance spectra within the visible range of the pigments most used in miniature painting, distempered in gum-arabic. The results obtained are such as to confirm the adoption of this method of disinfection.

Introduction

Since its origin, the production of miniatures has been wide and varied, but the technique seems to have scarcely evolved in the course of the centuries, as several publications confirm (1, 2, 3, 4).

In fact, if we consider the different times or places, we cannot observe any significant changes in the materials used by the miniaturist. The developments of this art can be ascribed rather to the manual ability of the artisan than to the use of improved materials (1).

The materials composing illuminated codices, parchment, organic pigments, binders and film substances suffer the degrading action of many different kinds of microorganisms.

Fausta Gallo and Alicia Strzelczyk (5) have studied the degradation of parchment and the frequency of this phenomenon on the works present in Italian libraries.

The microbiological attack examined by these researchers in certain cases seems to be particularly damaging since it is evidenced with difficulty; in fact, it has been observed that, in its first stage, the microbic development occurs inside the thickness of the parchment and later appears on its surface; it proliferates mainly where there is the highest concentration of biodegradable organic material.

In this case, the flaking of the colouring or the formation of stains represent only the final stage of the attack.

In order to inhibit the activity of the microorganism, one can resort to a sterilization in the gaseous state; this allows a better compenetration and contact of the biocide with the material to be protected.

On the other hand, it is very important to verify whether this biocide medium is liable to be fixed by the organic materials composing the work of art and consequently to alter their properties. The action of ethylene oxide has been sufficiently studied in relation to paper (6, 7, 8), but we know very little about the effects of this gas on colourings and especially on the binders used in laying the colours on parchment.

In fact, for this same reason, we have carried out an examination of the chromatic peculiarities of the main inorganic and organic pigments mixed with gum-arabic and exposed to the action of the same biocide.

The study on the materials, both untreated and treated with the chosen biocide, has ben carried out before and after artificial U.V. aging in standard conditions.

The following checks have been chosen:

- 1) Viscosity measurement, before and after the various treatments. The check was aimed at showing possible variations in molecular weight.
- 2) Adhesion measurement of the adhesive on an inert support (glass) before and after the various treatments.
- 3) Colorimetric measurements of the pigments considered before and after the various treatments.

1) Preparation of samples

The following materials have been considered:

a) parchment (manufactured by hand) prepared by the following technique: the parchment has been moistened with a sponge, then ^{and} it has been tautened and simultaneously fixed to a hard ^{and} flat support. It has been left to dry for 24 hours, taking care to prevent the formation of folds and wrinkles by further flattening.

Since the parchment presented a granular surface, it was then smoothed with emery paper and cleaned with alcohol.

Then the parchment was divided into rectangular samples measuring 2.5 by 3.0 cm for colorimetric analysis; these measurements have been chosen in relation to the size of the spectrophotometer sample-holder.

b) Adhesive materials: egg white, starch, casein, animal glue, gum-arabic.

b-1. Egg white: a mixture of 5g of egg white (Carlo Erba) and 100 cc of H_2O is homogenized with the magnetic stirrer for about 100 minutes and is then allowed to settle for 24 hours in a refrigerator at $5^{\circ}C$.

b-2. Starch: 20 g of F.U. ^{rice} starch (G. Faravelli) are distempered in 300 cc of H_2O . The mixture is then heated in water bath until it assumes a gelatinous aspect; after heating water is added to bring the mixture back to its original volume.

b-3. Casein: 20 g of casein (G. Faravelli) are distempered in 160 cc of an aqueous solution containing 6% of $(NH_4)_2CO_3$.

b-4. Animal glue: 50 g of "ATOM" animal glue in pills are left to swell in 600 cc of water for 24 hours. They are, then, heated in water bath until they dissolve and water is added up to the exact volume.

b-5. Gum-arabic: 2 g of F.U. gum-arabic (Carlo Erba) are mixed with 100 cc of H_2O . The mixture is then left to swell for 24 hours, mixing it now and then, and finally is filtered through an SS blackband filter.

In order to reproduce as far as possible the disinfection conditions of the binders, it is necessary to work not on the adhesives as they are but on the adhesives which have been first diluted following traditional recipes and then dried on glass slides and finally scraped off.

For the measuring of adhesion, each adhesive has been layed in a thin film onto a common glass slide of 10 by 10 by 0.3 cm using an automatic apparatus for the preparation of slides for thin layer chromatography; by this technique it has been possible to obtain standard films of the various adhesives with an average thickness ranging

from 10 to 20 μ .

In order to obtain the best adhesion of the adhesive substance to the support, the glass slides were previously treated with chromic mixture and with an alkaline detergent solution in order to remove grease, washed with distilled water and dried by exposure to air in absence of dust.

As for viscosimetric measuring, we have limited our research to gum-arabic and animal glue, since it was possible to obtain a good reproducibility of measurements only in relation to these two substances. In fact, the egg white, scraped off the glass slides, turned out to be practically insoluble in water, while the starch and the casein were only partially soluble.

So slides measuring 20 by 7.5 cm were covered with a layer of adhesive the same apparatus for thin layer chromatography.

After drying, it has been noted that gum-arabic detaches itself easily from the support since it has a low adhesive power to glass. The detached flakes with a thickness of 0.1 mm were put into Petri capsules, for the next operations.^(o)

c) Colours

The following colours have been employed:

Lapis Lazuli or Ultramarine Blue (Winsor & Newton).
 Azurite (natural product of unknown origin).
 Indigo (Carlo Erba).
 Litmus (Merck) (colouring principle produced from such lichens as Variolaria, Lecanora, Roccella).
 Green Earth (Winsor & Newton).
 Basic copper carbonate (Carlo Erba), or Malachite.
 Verdigris (B.D.H.), copper acetate.
 Indian Red (Winsor & Newton).
 Cinnabar (Merck).
 Rose Madder or Garance (Winsor & Newton).
 Carmine (I.C.N.).

^(o) Note: in the Middle Ages the binders most used in miniature painting were gum-arabic, egg white, and skin glue (4). In order to extend the results of this research to other uses, starch glue and casein have been also taken into consideration.

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Cochineal (product prepared in laboratory).
Braziline (B.D.H.).
Mosaic gold (product prepared in laboratory).
Realgar (Carlo Erba).
Saffron (Sidas, Padua).

The Winsor and Newton inorganic pigments, as well as those prepared in the laboratory, have been checked under the minerologic microscope and by an energy dispersive x-ray fluorescence using Tritium ^3H and Promethium ^{147}Pm sources. The cochineal and mosaic gold pigments have been prepared by the following techniques:

Preparation of mosaic gold (stannic sulphide): 4 parts of melted tin are added to 2 parts of mercury; 2 parts of sulphur and 2 of ammonium chloride are added to this amalgam; this is then heated on a Bunsen burner till a dark yellow pigment is obtained. The mass thus obtained is pulverized, washed with water and ground (4, 9, 10).

Preparation of the cochineal lake: 1 g of finely pulverized cochineal is added to 100 cc a 3.6% aqueous solution of sodium carbonate. This is allowed to settle for 2 hours and is then filtered. 14 g of alum powder are added slowly to the warm solution. When foam appears the addition of alum is suspended and the amalgam is filtered. The pigment obtained is washed with water and dried (11).

For painting the parchment samples, the above pigments have been distempered in gum-arabic since this adhesive material was one of the most used in miniature painting (4); furthermore, the use of this adhesive rendered the preparation of the samples more reproducible.

2) Treatment by ethylene oxide

The samples, prepared according to the above techniques, have been divided into four groups:

I group: "blank" samples, not to be treated;

II group: samples to be treated by U.V. aging only;

III group: samples to be treated by sterilization with oxide;

IV group: samples to be treated first by sterilization with ethylene oxide and then by U.V. aging.

The disinfection has been carried out in an autoclave (De Lama, Pavia) with a mixture of 88% of Freon-12 (methane dichlorodifluoro) and 12% of ethylene oxide, corre-

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sponding to 120 g of ethylene oxide per kg of gas.

The techniques and the quantities, based on data found in literature (6, 7, 12, 13) were the following:

Ethylene oxide concentration	= 500 g/m ³
Time	= 24 h
Temperature	= 30°-35° C
R.H.	= 50%

Once the books had been put into the cell, vacuum was obtained and the gas was introduced in the above quantities.(°)

3) U.V. aging

The aging has been carried out in a climatic chamber (Angelantoni) equipped with a lighting installation presenting the following emission spectrum:

at 200-300 m μ	100-140 lux
at 300-400 m μ	-----
visible range	220-250 lux

The aging conditions are as follows:

Time = 33 h for adhesion and colorimetric tests
Time = 75 h for viscosity tests
Temperature = 35°C
R.H. = 80%

Note: A preliminary problem was that of checking the penetration of gas into the adhesive films. To this purpose, in the Biological Laboratory of the Istituto Centrale per la Patologia del Libro, glass slides were prepared in Petri capsules inoculated with the following microorganisms:

Aspergillus niger
Trichoderma viride
Aspergillus flavus
Penicillium notatum
Chaetonium globosum

these slides were then covered with a layer of adhesive about 0.1 mm thick.

The same tests were repeated on parchment inoculated with the same microorganism. The disinfection gave positive results.

We wish to thank the Biological Laboratory of the I.C.P.L. for their cooperation.

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For colorimetric tests, the aging duration corresponds to the time necessary to obtain a complete colour change of the standard strips according to the Swiss standard S.N.V. 195-8-09 of 1966 (Soc. EMPA-G, Unterstrasse 11, St. Gallen 9001, Switzerland).

4) Measurement techniques and results

4-1. Viscosimetric measurements

We used capillary inverted viscosimeters of the Cannon Fenske kind (14).

The measurements have been carried out at 20°C. The viscosity values at various degrees of concentration of adhesive are recorded in tables 1 and 2 in figures 1 and 2.

Table 1

Gum-arabic kinematic viscosity in centistokes versus percentage of concentration in water.

Samples	Concentration				
	0,1%	0.5%	1%	1.5%	2%
Untreated	1.956	2.474	2.886	3.449	3.672
Treated with EtOx	1.998	2.342	2.994	3.398	3.919
Untrated-U.V.aging 75 h	1.864	2.201	2.564	3.010	3.372
Treated with EtOx, U.V. aging 75 h	1.886	2.331	2.623	3.079	3.300

Table 2

Skin glue viscosity in centistokes versus percentage of concentration in water.

Samples	Concentration			
	0.1%	0.5%	1%	2%
Untreated	1.888	2.227	2.849	5.080
Treated with EtOx	1.860	2.222	2.818	4.667

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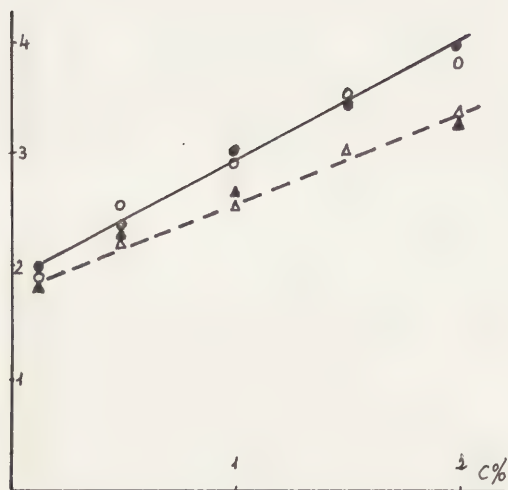


Fig. 1: Gum-arabic
viscosity

- Untreated
- Treated
- △ Untreated-aged
- ▲ Treated-aged

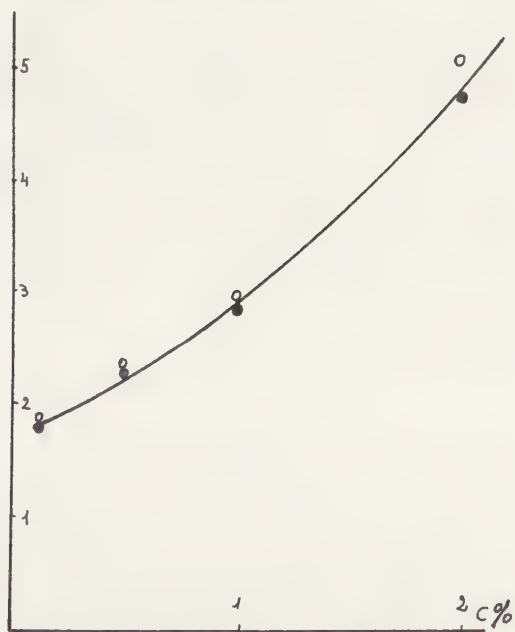


Fig. 2: Skin glue
viscosity

- Untreated
- Treated

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It has not been possible to carry out viscosimetric measurements on aged skin glue samples, since just half an hour's exposure to U.V. rays of this adhesive layed on slides was enough to render it partially insoluble.(°)

Note

Since we noted in the samples for viscosimetric measurements that the adhesives (especially gum-arabic) tended to yellow considerably after aging, it seemed interesting to check whether the ethylene oxide treatment was favouring this phenomenon.

We measured the brightness of Whatman paper samples treated with the adhesives considered: gum arabic and animal glue. In order to obtain an uniform treatment, the samples were soaked in the adhesive solution in the following conditions: 1/2 g of paper into 100 cc of solution containing respectively 3% of gum-arabic and 2% of skin glue.

For measuring the brightness we used the Photoelectric Reflection Meter, Mod. 610 of Photovolt Co., using a 600 W research unit with a Kodak Wratten 49 filter.

The results obtained are recorded in the following table:

Brightness of adhesive soaked paper treated with ethylene oxide.

Samples	unaged		U.V. aged 96 h	
	untreated	treated with ethylene oxide	untreated	treated with ethylene oxide
Whatman	86	87	71	70
Whatman + gum-arabic	87	86	71	70
Whatman + skin glue	87	86	73	74

The above table shows the decrease in brightness after aging; however, no relevant differences are to be found between samples treated or untreated with EtOx.

4-2. Adhesion measurement

Adhesion measurements have been carried out using the so-called method of "perpendicular cutting" with an apparatus already employed for checking adhesives (14,15).

This apparatus obtains on a film of adhesive a series of parallel cuts in a certain direction and a second series at right angles to the first.

The operations carried out were as follows:

- a) measuring of the thickness of the film of adhesive in hundredths of millimeters;
- b) measuring of the minimum load required to obtain cuts through the adhesive film to the underlying glass support;
- c) carrying out a series of perpendicular cuts with the load established in b) so as to obtain a grid measuring 0.8 by 0.8 cm and divided into 100 squares;
- d) application of a 3M adhesive tape onto the grid and its subsequent tearing off using a traction force perpendicular to the adhesion surface;
- e) counting, under the microscope, of the adhesive squares left undamaged; this number represents directly in percentage the adhesion measurement. Furthermore, we calculated the relative adhesion of the samples compared to that of the sample presenting the best adhesion percentage (maximum value) to which we assigned the value 100.

In tables 3, 4, 5 we recorded, for each treated and untreated binder, the values respectively of the minimum load required for cutting the film, of the adhesion percentage and of the adhesion percentage relative to the maximum value, for each series.

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Table 3Measuring of the adhesion percentage of egg white

Samples	load required g	adhesion (%) and adhesion relative to the max. value (%)	average adhesion
Untreated	1000	100.0	94.9
		90.5	
		96.0	
		93.0	
Treated with EtOx	1000	91.0	91.9
		86.0	
		97.0	
		93.5	
Untreated, U.V. aged	1000	88.0	83.0
		82.5	
		78.5	
Treated with EtOx, U.V. aged	1000	89.0	76.3
		65.5	
		81.5	
		69.0	

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Table 4Measuring of the adhesion percentage of rice starch

Samples	load required g	adhesion %	average adhesion	adhesion % relative to the max. value
Untreated	2750	99.0	93.5	100.0
		88.0		88.9
		94.5		95.5
		92.5		93.4
Treated EtOx	2250	95.0	96.2	96.0
		98.5		99.5
		98.5		99.5
		98.5		99.5
		90.5		91.4
Untreated U.V. aged	2000	95.0	93.5	96.0
		95.5		96.5
		94.5		95.5
		89.0		89.9
Treated EtOx, U.V. aged	2250	91.0	91.9	91.9
		87.0		87.9
		96.5		97.5
		93.0		93.9

Table 5Measuring of the adhesion percentage of casein

Samples	load required g	adhesion %	average adhesion	adhesion (%) relative to the max. value
Untreated	2850	70.0	67.8	74.5
		73.5		78.2
		53.5		56.9
		94.0		100.0
		48.0		51.1
Treated EtOx	2850	66.5	61.5	70.7
		65.5		69.7
		55.0		58.5
		59.0		62.8
Untreated U.V. aged	2850	53.0	60.4	56.4
		56.5		60.1
		64.0		68.1
		71.0		75.5
		57.5		61.2
Treated EtOx, U.V. aged	2850	61.5	52.4	65.4
		51.0		54.3
		56.5		60.1
		64.5		68.6

4-3. Colorimetric measurements

We have used an OPTICA CF4R double beam recorder spectrophotometer equipped with an accessory apparatus for reflectance measurements. Spectra have been obtained between 400 m μ and 700 m μ compared to a standard of magnesium oxide.

We have determined the reflectance spectrum of samples obtained with pigments distempered in gum-arabic on a 2.5 by 3.0 cm parchment support. We compared, for each colour examined, the spectra a) of untreated and EtOx treated samples and b) of untreated - U.V. aged and EtOx treated - U.V. aged samples. We found only slight variations in the reflectance values, most evident in the case of aged samples. However, we must take into account that the painted parchment samples present some differences specifically due to their manufacture by hand.

Since it would be impossible to reproduce all the diagrams obtained, we show in figures 3 and 4 the reflectance spectra of some colours, both treated and untreated after aging, since this comparison seems to best underline the results of the measurements.

Conclusion

If we examine the relative viscosity values at the various concentrations in water of gum-arabic and animal glue, we can conclude that the ethylene oxide-disinfection treatment, carried out according to the techniques described above, hasn't determined significant variations in viscosity.

We can draw the same conclusions in relation to the brightness of the above substances.

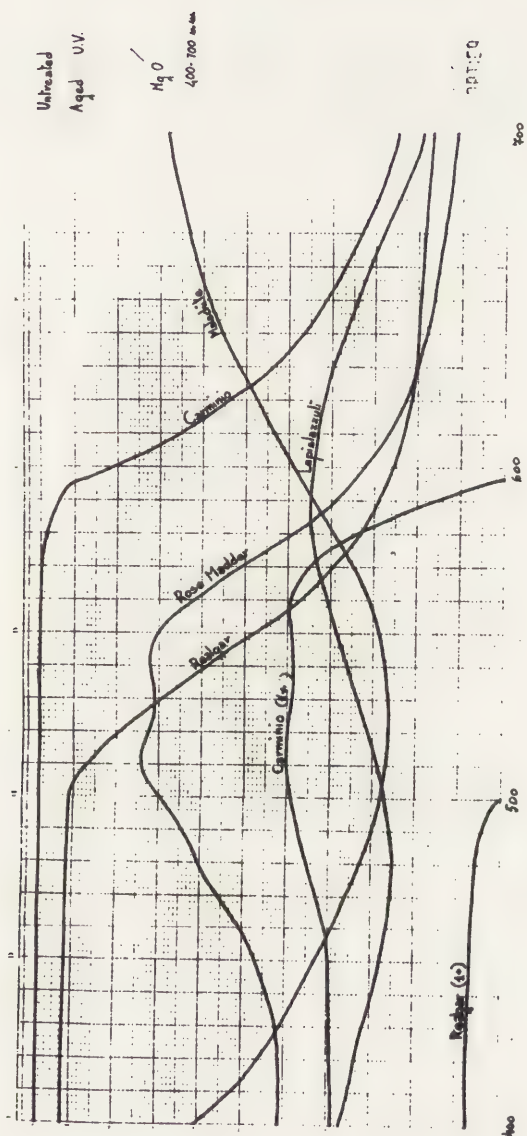
As for adhesion, in relation to casein and egg white, we can note a difference in behaviour between the samples treated with ethylene oxide and the untreated ones; on the contrary, there are no significant differences concerning rise starch.

As regards the colorimetric measurements of the untreated and treated colour samples, we may conclude that no significant chromatic variations have occurred.

In the few cases in which the instrument recorded slight differences between the various samples, these can be ascribed to the dishomogeneity of the parchment supports.

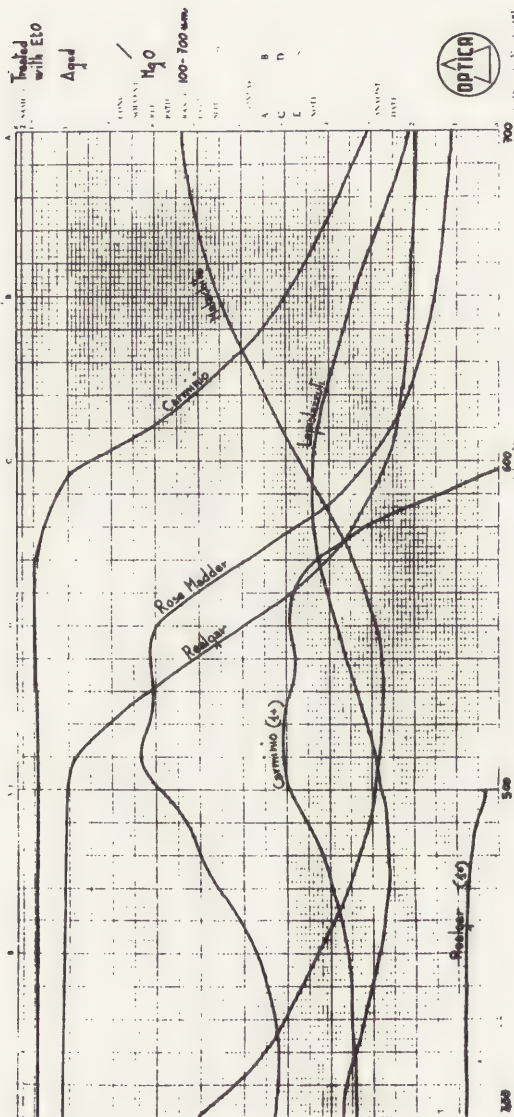
Finally, we can conclude that the ethylene oxide treatment determines slight variations in the adhesion

fig. 3



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Fig. 4



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percentage only in two substances. On the whole, the results, even if not definitive, can be considered significant and sufficiently encouraging as far as the ethylene oxide disinfection of infected materials is concerned. However, the ethylene oxide treatment shouldn't be employed indiscriminately, but only in those cases in which the microbiological attack is present and represents a real danger to the conservation of the piece of art.

Acknowledgement

We wish to thank mister D. Artioli for his valuable aid in preparing samples and measuring viscosities.

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REMOVAL OF GENERAL SOILS AND PIGMENT
SPOTS FROM PARCHMENTS

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REMOVAL OF GENERAL SOILS AND PIGMENT SPOTS FROM PARCHMENTS

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Parchment is known to be an extremely durable and lasting material which has made it possible to preserve the most ancient manuscripts and documents up to the present time. However, as a result of natural aging and, especially, of unfavourable conditions for preservation it is damaged in different ways. Frequent damages include general soils and pigment spots of microorganisms. There are comparatively few works devoted to cleaning; they usually contain the most general recommendations which lack the necessary methodological guidance. In particular, these works suggest that spots from thin parchments of bindings can be removed by cleaning them with a sponge wetted in water with a slight addition of glue, but the concentration and nature of the glue are not mentioned; it can only be supposed that what is meant is water solution of gelatin. If parchment is rendered impure with mineral or organic substances, it is recommended that it should be cleaned with water, soap alcohol, a weak solution of soap or an alcohol solution of the mixture of borax and boric acid with a slight addition of an antiseptic--nipagin. In case there are yellow and brown spots, some authors suggest that parchment should be carefully treated with hydrogen peroxide, a water solution of alum or chlorine water, followed by careful washing and neutralization of whitening agents. All surface soils in the form of mycelium and spores of fungi, adipose matter and other substances are carefully removed mechanically and then disinfected. Large size documents have an insertion of paper sheets of appropriate size, impregnated with fungicide. This method is particularly useful in case a manuscript should be constantly protected for a long period of time.

Analysis of literature shows that the works devoted to the removal of soils from parchments are, as a rule, purely practical and do not contain sufficient information on possible structural and mechanical, and physico-chemical changes of the material to be cleaned. Since it is necessary to establish reliable, scientifically grounded restoration methods, we have explored the possibility of making general cleaning and removing pigment spots of micro-organism nature from parchment manuscripts and bindings.

Objects of investigation were parchment bindings of the 17th-19th centuries, made in different ways, and old parchments with texts. Since all parchments possess some alkalinity, the choice of cleaning and whitening systems depended to a great extent on their hydrogen content, the change being allowed within the 7-10 range. Water, alcohol and water alcohol suspensions of subalkali soap, ammoniacal-alcohol soap paste with a slight addition of borax, and water solutions of chloramine B were tested as cleaning and whitening agents.

The parts of the parchments that have been soiled were treated with appropriated cleaning means, after which they were washed with water or alcohol; all the treated samples were dried in a press. To remove pigment spots parchment was placed on glass, cleaned with gauze tampon wetted with chloramine solution; then two or three layers of gauze also impregnated with chloramine, polyethylene film, glass and a small weight were placed on it. In case of through spots a compress was put on both sides of the parchment. In case of need gauze was again wetted in the process of whitening. The overall duration of whitening amounted to 1-5 hours depending on the thickness and quality of whitening material, the intensity of the spot or soils, and demands made on the degree of cleaning. The cleaning and whitening effect of the systems under investigation was assessed in an organoleptic way. The protection of texts and fixing of borders of cleaned areas were ensured with fluorolon H6.

Water, alcohol suspensions of soap and ammoniacal-alcohol

soap paste with borax are inactive enough towards parchment, the probability of their effecting the parchment properties being practically the same, because the use of the two latter systems shall be followed by water or alcohol washing. The use of chloramine naturally presupposes the possibility of physico-mechanical and physico-chemical changes in parchment, as prolonged action of the alkali system can lead to hydrolisis of collagen, the main albumen making up any leather, and parchment, in particular. In this connection we studied the effect of whitening with chloramine on tensile strength, elasticity (relative elongation), hygroscopicity, moisture yield and acidity of parchments both right after treatment and after artificial aging. The characteristics of parchments were determined in accordance with standard methods accepted for leathers. Rapid aging was effected with ultraviolet illumination for 200 hours.

The investigation showed that all the tested systems can be used for general cleaning of parchments, the most effective being paste and chloramine. After being treated with paste, parchments acquire a lighter colouring. If cleaned with chloramine, the colouring becomes lighter.

In case of prolonged treatment with chloramine (whitening), intensely coloured, through pigment spots can be removed; if texts are fixed beforehand, general soils of bindings and manuscripts can also be removed. Whitening with chloramine practically does not affect physico-chemical properties or the value of pH of parchments either in ordinary conditions or in case of rapid aging. This testifies to the fact that various soils of parchments can be removed, their durability remaining unchanged.

In conclusion, it should be pointed out that in view of the great variety of parchments and of the nature of their soils, a differentiated approach to the choice of means and methods of cleaning should be adopted. A preliminary sample should be made for each parchment document to be restored, as the materials ensuring the positive effect in a certain case can lead to undesirable results in another one (for instance, some parchments can turn yellow due to the effect of chloramine).

78/14/12

THE SUBSTITUTION OF NATRIUM
PENTACHLOROPHENOLAT WITH OTHER
ANTISEPTICS IN THE RESTORATION
OF PAPER

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Zagreb, 1978

THE SUBSTITUTION OF NATRIUM PENTACHLOROPHENOLAT WITH OTHER
ANTISEPTICS IN RESTORATION OF PAPER

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The conservation of historic and artistic works was always very important for all the humanity. That's why the restorers from many countries are studying this problem of conservation very carefully. In the USSR each year offers wider possibilities for usage of chemistry and chemical materials in restoration and conservation of art works and cultural as well as historical monuments.

Many physical and chemical factors affect the conservation of artistic works: sharp fluctuation of temperature and humidity, UV-rays, ozone gases which litter the air, hydrogen sulphide, ammonia, sulphur dioxide, nitric oxide, fermenting chemical reactions, accelerating the processes of ageing; and biological factors: lichens, water-plants, bacteria, mouldy fungi.

Mouldy fungi do great damage to artistic works, especially in the tropical countries. However, there are mouldy fungi in the countries of moderate climate zone too. For example, mouldy fungi appeared at the varnished surface in Greenland. Mouldy fungi damage variously: they can completely deform some materials, intensifying the diffusion of liquid through the isolated parts, mar the surfaces of materials. The most great destruction occurs with materials which consist of nutrient medium for mouldy fungi: sizing of paper, canvas.

The various products secreted by the microorganism in its vital activity process destroy the artistic works too. When there are sufficiently nutrient medium and oxygen mouldy fungi can accumulate sorrel acid, lemon acid, amber acid, in the nutrient medium. Organic acids oxidate the medium and change the colours because the pigments used in painting have indication properties and their colours depend on PH of the medium. The pigments secreted by the mouldy fungi in their development promote the appearance of the indelible spots on the painting. It concerns above all the family of Dematiaceae.

Infection of the works is the result of the spores of fungi, catching the surface of the painting; or when the works infected by the mouldy fungi come into contact with healthy works. Often the spores of fungi are already in the initial materials: paper, canvas, colours. Sometimes the infection is the result of the internal films of colours, which come already infected in the painting process.

It is easier to prevent development of mouldy fungi than to struggle with them. It is therefore necessary to create conditions for conservation: normal temperature and humidity, and selection of chemical substances-antiseptics, protecting the works from biological destruction.

Formalin and phenols are recommended abroad for treating the works. In our country in the restoration of paper natrium pentachlorophenolat is used as a concerning agent of a wheaten glue. However this substance has a number of defects.

1. It is a strong lachrymator, because it provokes inflammation of mucous membrane.

2. It gets dusty in the process of weighting.

3. It grows brown with time.

4. It is easily pitched.

5. It has an unpleasant odour.

6. It stains glue films and lining materials.

Natrium pentachlorophenolat has been used as antiseptic in the restoration of paper until recently and as a result the new spores of mouldy fungi appear there. And they can grow at the glue, protected by this antiseptic. All these defects make natrium pentachlorophenolat unacceptable in the restoration practice.

Because we conserve the historic and artistic works, the chemical substances which we use, must correspond to the following demands:

1. Wide spectrum of effect.

2. Innocuous for the human health.

3. Indifferent to the painting and paper pigments.

4. Colourlessness and indifferentness of mediums.

5. Soluble in water and spirits.

6. Not destroy the artistic works.

We have found only one substance corresponding to all demands. It is 'nypagin' - methyl paracept of paraoxibenzoic acid (molecular weight 152,5). It is a white powder without any odour and any taste, endurable to heat and cold

Nypagin is used in Italy for conservation of meat and fish products. In Norway it is used for protection of biological infections in confectionery. In our country nypagin is used in food and cosmetic industries as a conserving agent for fat compounds. That's why we decided to try nypagin in the restoration of paper as a conserving agent of a wheaten glue instead of the pentachlorophenolat.

The work consisted of some stages. At first we determined comparative activity of nypagin and pentachlorophenolat at the pure cultures as a test-organism. The following fungi from the works of paper were taken as a test-organisms: *Penicillium puberulum*, *Penicillium chrysogenum*, *Aspergillus flavus*, *Aspergillus repens*, *Aspergillus versicolor*, *Mucor rocemorus*, *Alternaria tenuis*, *Trichoderma lignorum*, *Cephalosporium acremonium*, *Cladosporium straminicola*.

The results of the experiments with the pure cultures gave favourable conclusions concerning the activity of nypagin. So we went on to check it on the material.

For the checking of the protective properties of the antiseptic all compounds of the works of paper was subjected. Nypagin was examined as a conserving agent with all type of papers (Whatman, drawing paper, news-print) and with all techniques of painting (water-colour, gouache, crayon, aniline dye).

For examining how the works would change with time under effecting of the antiseptic used all samples were subjected to the process of ageing, which is used at the

Leningrad Factory of Artistic Colours, under mercuric-quartz lamp PRK-2 during 500 hours. For defining the behaviour of pigments under the long-run effect of anti-septics, the samples were subjected to spectrophotometry at SF-10 before and after the process of ageing. The degree of changing of spectral curves, which characterize the colour of the samples, indicates the changes, which occurred in the process of ageing.

The experiments were done in strict conditions at relative air humidity (95%) and temperature 27°C - the optimum temperature for the development of the most mouldy fungi. For this purpose the lid of Petri scutum with an infected sample, treated with a verified anti-septic before it, was set in the Koch scutum. Then some sterile distilled water was poured out at the bottom of the Koch scutum for creating the higher relative humidity. All this was sustained in the thermostat at 27°C during 3 months. The experiments of conservation of samples proved the favourable activity of nypagin as anticeptic.

It does not give in to natrium pentachlorophenolat. The study of the effect of nypagin on all compounds of the grafic works demonstrated that it doesn't make any change even at such naughty materials as wood paper and aniline dye.

The experiments brought us to do the following conclusions:

- 1) The wheaten glue and the duplicating material don't grow yellow when treated with nypagin. Natrium

pentaclorophenolat makes it grow yellow.

2) Nypagin is indifferent to all pigments used in the restoration of graphic.

3) Nypagin doesn't provoke any change of optical properties at the ageing process.

4) Nypagin is innocuous for human.

5) Nypagin is colourless.

6) Nypagin has no odour.

7) Nypagin doesn't get dusty in the process of weighting, it is safety.

8) Nypagin doesn't grow brown while storing and doesn't decompose under the light.

9) It has a neutral medium of solutions.

10) It is soluble in ethane, in ether and propylene-diethylglycol.

11) It is stable to heating.

The evident advantages of nypagin permits us to recommend it as a conserving agent for wheaten glue in the restoration of grafic works.

Nypagin is produced by the Moscow 'Synthetic Fabric'. There is an instruction for the use of nypagin of the basis of these experiments.

Nypagin - p-oxybenzoic acid methyl ether - is used in the restoration practice at the Russian Art Restoration Centre after I.E.Grabar from 1973. All experiments give very good results.

78/14/13

BIODESTRUCTION AND BIOSTABILITY
IN LIBRARY MATERIALS

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BIODESTRUCTION AND BIOSTABILITY IN LIBRARY MATERIALS

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There are over 300 species of fungi causing damage to library stocks. Owing to the process of evolution, the fight against their destructive action is growing more and more complicated. A differentiated system of protection has been worked out to increase the biostability of printed matter and manuscripts (or to make printed matter and manuscripts more proof against biological change or to increase the resistance of ... to biological change): a) conservation in the usual storage conditions; b) protection from the effect of temporary increase in humidity and temperature; c) the imparting of greater biostability during exposure to prolonged unfavourable influences. In selecting the preservatives, account is taken not only of the commonly accepted requirements, but also of the capacity of biocides to combine with other materials to provide durability of paper, and of the changing microstructure of the paper under the influence of these compounds, and of their specific influence on the various microfungi, etc. Preference is given to polymeric substances. In the USSR a new polymeric antifungal substance is being synthesized - a guanadin derivative which has been tested exhaustively in the laboratory of the Saltykov-Schedrin State Public Library. Its advantages as a preservative have been proved. The subject of this paper is the use of this substance for the protection of library materials.

Books and documents are complex chemical combinations of both natural origin and of artificial and

synthetic polymers. During storage they undergo the processes of aging, alteration and destruction. This leads to the appearance of new destructive substances in their composition. Over 300 species of fungi have accommodated themselves to living on these materials. the process of evolution has led to an increase in the number of organisms which have made paper their habitat.

Books undergoing restoration are combined with materials that are more or less similar to the original. With the years, more and more techniques appear, using new chemically synthesized polymers to restore the damaged properties of the objects in question, and to imbue them with new properties. This corresponds to the general trends in contemporary restoration.

The restorer, nonetheless, is always desirous of using natural amterials and of interfering as little as possible in the original composition (structure?) of manuscripts and ancient books. Many of the materials used, particularly the adhesives, are aqueous systems, in which the content and form of the water changes easily in accordance with the level of relative humidity of the air. In restoring paper, the use of hydrophilic compounds has proved to be reliable, being compatible with its colloidal system. It is mainly these compounds that are subject to biodeterioration. Therefore the problem of susceptibility, protection and biostability of objects of cultural value always takes first priority with researchers. However, it can never be solved completely or simply. This is due to two reasons: one, the fact that the organisms adapt themselves to living on materials containing antifungal substances, and that this process is endless and has, so far, not succumbed to prognosis. Two, more and more is required for biostability as a result of the constant widening choice of chemicals used for restoration

purposes. The history of restoration records the fact that preservation of the first adhesives was only required to act for a few days, while the work was going on. Subsequently the task was complicated by the necessity to give protection not only to the adhesive, but to the objects being restored too. This led to the use of higher concentrations of antifungal substances. and to the rejection of some of them. Later on, rigid standards were established for substances to be used for conserving valuable writings and printed matter. Meanwhile things were happening that influenced restoration work in the whole world. At the same time the range of activity in the field of protection of objects of cultural value was widening. The system of biological protection was subdivided along three main lines:

1. Conservation of the parts of the objects (these parts are mainly adhesives) most susceptible to the action of microorganisms, for the purpose of ensuring their conservation in ordinary storage conditions;

2. Conservation of objects with a view to protecting them in an emergency, when some accident temporarily upsets normal storage conditions;

3. Conservation providing for the protection of objects from prolonged exposure to damaging elements: sudden changes in temperature and humidity, repeated periods of high temperature and high humidity.

In practice there is, naturally, no such strict differentiation. Many protection systems are transitional.

In the new conditions for library activities we consider it advisable to implement restoration and conservation processes that simultaneously solve the problem of durability, biostability and resistance to wear. From this point of view optimal results can be achieved

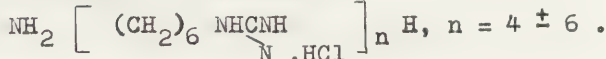
by the use of mainly polymer compounds that combine well with material of natural origin.

Our work may serve as an example of this. We used polymeric guanidine compounds for the protection of adhesives and the paper of manuscripts and printed matter.

Guanidines are derivatives of imino-urea. The formula for guanidine is $\text{HN}=\text{C} \begin{smallmatrix} \nearrow \text{NH}_2 \\ \searrow \text{NH}_2 \end{smallmatrix}$. It is a strong base, it has the same strength as NaOH. One of the guanidine derivatives arginine, occurs in protein. The formula for natural guanidine derivative (isemilene-guanidine) is $\text{HN}=\text{C} \begin{smallmatrix} \nearrow \text{H}_2 \\ \searrow \text{NHCH}_2\text{CH}=\text{C}(\text{CH}_2)_3 \end{smallmatrix}$;

The seeds and leaves of broom contain it.

Polymeric guanidine compounds are more stable than monomers and have a number of useful properties. Some of them have been developed in the USSR /Гембицкий П.А. и др., 1975/. For example, polynexamethyleneguanidine - a water-soluble polymer of the cation type. Its chemical structure is



HCl may be replaced by other acids, among them lauric acid. This substance is a transparent, hard, yellowish, odourless resin with a softening temperature of 80 - 100°C. The resin is hygroscopic, water-soluble, any concentrations are possible and is 1% water solution of polynexamethyleneguanidine has pH 8-10, stable in storage. Alkaline pH is caused by basic groups NH_2 . When heated for a short time and on sunlight the polymer does not change its properties. In decomposition polymeric carbamide (urea) $(\text{NH}_2 - \text{CO} - \text{NH}_2)_n$ and NH_4Cl are formed. And so polyhexamethyleneguanidine does not have a bad influence on the physical- and chemical state and properties of paper during arti-

ficial aging and prolonged storage. Owing to its polymeric structure and kationic properties polyhexamethyleneguanidine is regularly spaced in the material. A microexamination of paper impregnated with polyhexamethyleneguanidine shows that the substance fills the spaces between fibers evenly and covers the fiber surface completely. Polyhexamethyleneguanidine has a fungicidal and fungistatic actions on book damaging fungi

/Нюкова Ю.П., 1972/. These fungi do not grow on paper which contains 1% of the substance: *Chaetomium globosum* Kunze ex Fr., *Penicillium cyclopium* Westling, *P. roquefortii* Thom, *Sporotrichum bombycinum* Cda., *Aspergillus terreus* Thom, *A. amstelodami* (Mang.) Thom et Church, *Verticillium tenerum* Nees ex Lk., *Myxotrichum deflexum* Berk., *Stachybotrys chartarum* (Ehr. ex Lk.) Hughes. The conidio spores of *Penicillium purpurogenum* Stoll, *Trichoderma viride* Pers. ex FR. perish. *Rhizopus nigricans* Ehr. ex Cda., *Aspergillus flavus* Lk. ex Fr., *A. niger* v. Tiegh., *Myrothecium verrucaria* (Alb. et Schw.) Ditm. ex Fr. need higher concentrations of polyhexamethyleneguanidine, up to 1.5-2% and even 3%.

The paper samples impregnated with a 2% solution of the polymers upon pH Level 8.5 showed themselves fungi-resistant under controlled conditions at relative humidity of 100%. This protection of the materials is ensured under accident conditions.

A valuable property of polyhexamethyleneguanidine is its compatibility with other polymers including proteins. The latter reduce the fungi retardation effect only 1.5-2 times. While it is known that in the presence of proteins other (monomeric) substances reduce their antifungal effect dozens of times. In connection with this the use of 1.5-2% preparation is advisable for conservation of water compositions containing protein and starch. The pH level of paper restored with this adhesive is 5-5.5.

Polymerous guanidine derivatives are compatible with the polymers which strengthen the paper and impart hydrophobic nature to it: polyethylenimine /Гамбицкий П.А., Жук Д.С., Каргин В.А., 1971/ polyamidamine, polyacrylamide /Савицкая И.Н., Холодова Н.Д., 1969/ and other modifications of these polyelectrolytes. The latter form complexes with cellulose and polyhexamethyleneguanidine. This improves the retention of the substance in the paper during moulding and water processing during restoration.

Cotton paper (48° Schopper-Riegler freeness, mass of 1 m² 40 g) containing polyhexamethyleneguanidine, polyamidamine and polyacrylamide was developed in the laboratory. Its structure and test results of the paper samples are shown in Table I.

Table I

Polymer		Number of paper sample, paper composition								
Name	Concentration, %	1	2	3	4	5	6	7	8	9
Polyhexamethylene-guanidine	1					x	x			
	2	x						x	x	
	3		x							
Polyacrylamide	1			x		x		x		
Polyamidamine	1				x		x		x	

Properties of paper samples

pH	6.6	6.6	6.6	6.5	6.5	6.4	6.4	6.3	6.3
Folding strength, number of double folds	28	31	168	215	186	223	238	256	16
Bioproofness, relative retain of strength, div.	2	2	5	6	7	8	7	8	1
Moisture content, %	4.4	4.7	5.0	4.9	4.1	4.8	4.2	4.2	4.7

The results summarized in Table I show that pH level of the laboratory-made paper is equal to 6 or a little bit more. In spite of the distinct alkaline reaction of a 1% initial product solution the low pH of the paper indicates that the suggestion of binding its amine groups to cellulose is correct. Polyhexamethyleneguanidine (samples 1,2) does not impart durability to paper. In the presence of polyacrylamide and polyamidamine (samples 3-4) folding strength increases 5-7 times, biostability being satisfactory (better than other samples show). The biostability was evaluated by means of the cellulases of *Trichoderma viride*.

Polyhexamethyleneguanidine did not increase moisture content of paper. The filter paper impregnation with 1.5% polyhexamethyleneguanidine solution led to a decrease in its moisture content from 46.7% to 17.7% at air RH of 100%, i.e. 3 times. When the humidity of the air is 45-50% the moisture content of this paper impregnated with adhesives based on NaCMC, polyvinylalcohol, polyvinylacetate became lower after introducing polyhexamethyleneguanidine into the paper composition.

The considerable increase of durability was achieved by means of paper impregnation with a 1% polyacrylamide solution and a 2% polyhexamethyleneguanidine

solution in strict succession. The paper became 20 times more durable and obtain biostability. If paper contains even 5% of polyhexamethyleneguanidine the character of its luminiscence under the influence of mercury line radiation with wave-length 365 nm remained unchanged. Polyacrylamide and polyamidamine impart luminiscence of a dingy-pink tint to paper.

Thorough hygienic and toxicological tests /Скворцова Е.К. и др., 1974; Скворцова Е.К., Нехомшева А.Г., 1974/ of polyhexamethyleneguanidine have been carried out. It was considered to be safe for the warm-blooded animals and applicable in medical practice.

CONCLUSIONS

The antifungal substance polyhexamethyleneguanidine has been proved safe for paper and may be used for restoration of library materials of any value. Polyhexamethyleneguanidine has regularly spaced distribution in paper. It does not increase paper moisture content. The substance supports biostability of paper and of natural compositions containing protein and starch for 2-3 years. It is notable for its specific action on cellulose-deteriorating fungi and inhibits the activity of their cellulases. At the same time it does not inhibit the effect proteinase and amilase which are used in restoration. Polyhexamethyleneguanidine does not change paper durability, but in combination with polyacrylamide and polyamidamine it increases paper permanence and resistance to wear considerably. Content of the antifungal substance does not prevent subsequent optical and photographic researches of documents. Labour and health protection of those working with polyhexamethyleneguanidine or using the documents processed with it is guaranteed.

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MICROBIAL PROBLEMS IN PHOTOGRAPHIC
PRINT COLLECTIONS

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MICROBIAL PROBLEMS IN PHOTOGRAPHIC PRINT COLLECTIONS

E. Czerwifiska and R. Kowalik**Abstract**

Different species of fungi destroying black-and-white photographic prints were isolated and partly identified. Photographic prints can be protected against microflora by immersing prints during 3 minutes in 1 per cent water solution of Hyamine 1622 or 0,5 per cent water solution of sodium salt of 4-chlore-3-cresol. The solutions should be prepared in distilled water.

Photographic prints are documents made on paper covered with a thin emulsion layer composed of gelatin and silver salts or other light sensitive chemical compounds.

Photographic print collections stored under conditions of relative humidity higher than 60 per cent and temperature of 24-26°C are liable to damage by air-borne spores of fungi and Actinomyces, which may utilize the gelatin in the emulsion layer as carbon and nitrogen sources. Silver salts and other compounds in the emulsion do not inhibit sufficiently the growth of microflora.

The growth of fungi and Actinomyces colonies occur

on the print surface and cause coloured or dull spots. As further consequence of the metabolism of microflora a complete destruction of the image and emulsion layer and a decomposition of the paper support may take place. Therefore it is necessary to protect photographic print documents against damages caused by micro-organisms, by ensuring proper storage conditions, or by treatment with biocides. According to the propositions of Kodaks Customer Service Pamphlet AE-22. Notes on Tropical Photography 1970, 1 per cent of Hyamine 1622/diethylbenzyl-tert-octylphenoxylethyl ammonium chloride/ protects black-and-white prints against harmful effects of fungi.

Experimental part

The study of the problems of protection of photographic prints by utilizing biocides against micro-organisms was started in our laboratory because climatic conditions in Poland and possible failures in air conditioning installations may favour a prolific growth of microflora. At first the micro-organisms, that destroy black-and-white photographic prints were isolated and identified with the use of different cellulosic media.

The next stage of our work was to investigate preventive methods for the protection of photographic prints. Hyamine 1622 and the sodium salt of 4-chloro-3-cresol, both in 1 per cent solutions in water were used.

The experiment was carried out in the following way:
50 x 50 mm squares of photographic prints were cut out with a sterile tool and placed in 100 mm Petri dishes on glass sticks:

-1/3 of the number of prepared samples was sprayed with sterilized distilled water

-1/3 of the number of samples was sprayed with Greathouse, Klemme, Barker medium/Ind. Eng. Chem., 14, 614/1942/ of the following composition

K_2HPO_4	1,3940 g
$MgSO_4$	0,7395 g
NH_4NO_3	1,006 g
$CaCO_3$	0,005 g
$NaCl$	0,005 g
Fe, Zn and Mn as SO_4 salts	0,001 g
distilled water	1000 ml

and 1/3 was sprayed with a suspension of spores of *Aspergillus niger*, *Aspergillus terreus* and *Penicillium brevi-compactum* in Greathouse, Klemme, Barker medium.

One half of every kind of the mentioned sprayed samples was dried in closed Petri dishes at room temperature.

The other half was kept in humid conditions most favorable for the growth of micro-organisms. For this purpose 10 ml of distilled sterilized water was pipetted to the bottom of Petri dishes/under the tested sprayed samples/; the dishes were closed and incubated at the

temperature 24-26°C.

After 3 days, samples dried at room temperature, as well as those maintained in humid atmosphere, were immersed for 3 or 5 minutes at 0,5 per cent or 1 per cent water solution of Hyamine 1622 or sodium salt of 4-chloro-3-cresol. Comparative samples were immersed in sterilized distilled water during 5 minutes.

All samples as well those treated with biocides as with sterilized distilled water only, were placed in 100 mm Petri dishes on glass sticks and dried for 48 hours at room temperature. Then they were transferred to 100 mm Petri dishes on potato-dextrose agar medium prepared from 1000 ml of water extract of 200 g of sliced potato + 17 g of agar-agar + 20 g of glucose. The assessment was made after 10 days incubation at the temperature of 24-26°C and 90 per cent of relative humidity.

Results

In the course of our test with black-and-white photographic prints the following fungi were isolated and identified:

Acrostalagus cinnabarinus Corda var. *nana*

Oudemans

Alternaria tenuis Nees

Aspergillus amstelodami Thom and Church

Aspergillus candidus Link

Aspergillus flavus Link

Aspergillus fumigatus Fresenius
Aspergillus niger van Tieghem
Aspergillus terreus Thom
Chaetomium globosum Kunze
Chaetomium ochraceum Tschudy
Fusarium probably *oxysporum* Schlechtendahl
Isaria Persoon ex Fries
Paecilomyces varioti Bainier
Penicillium brevi-compactum Dierckx
Penicillium sp.
Rhizopus sp.
Scopulariopsis brevicaulis Bainier
Spicaria violacea Abbott
Trichoderma album Preuss
Trichoderma viride Persoon ex Fries
Trichothecium roseum Link

and some species of *Streptomyces*

The results of experiments on the protection of black-
and-white photographic prints against micro-organisms
 concern as well the dried samples as the ones incubated
 after spraying with sterilized distilled water, Great-
 house medium and or a suspension of spores of fungi in
 Greathouse medium.

According to these data the growth of fungi was not ob-
 served on photographic print samples and on the medium
 after a 3 minutes period of immersion in 1 per cent
 water solution of Hyamine 1622 or 0,5 per cent water.

solution of sodium salt of 4-chloro-3-cresol. The immersion of photographic print samples in 0,5 per cent water solution of Hyamine 1622 even for as long as 5 minutes was not sufficient to destroy the micro-organisms, which are able to vegetate on the surface of the sample. This was experimentally confirmed by the growth of fungus on potato-dextrose agar medium with samples, which were:

sprayed with sterilized distilled water, dried or maintained in conditions suitable for the vegetation of microflora, and then immersed during 5 minutes period in 0,5 per cent water solution of Hyamine 1622.

It is worth mentioning that the growth of fungi on the samples treated with 0,5 per cent water solution of Hyamine 1622 was much less than on comparison samples immersed in distilled water.

On the basis of our experiments it may be concluded, that black-and-white photographic prints can be protected against microflora, which develop on them, by immersing prints during 3 minutes in 1 per cent water solution of Hyamine 1622 or 0,5 per cent water solution of the sodium salt of 4-chloro-3-cresol. The solution should be prepared in distilled water.

CONTRIBUTION TO THE PROTECTION OF AUDIO-
VISUAL RECORDS AGAINST DESTRUCTIVE MICROFLORA

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5th Triennial Meeting
Zagreb, 1978

CONTRIBUTION TO THE PROTECTION OF AUDIOVISUAL RECORDS
AGAINST DESTRUCTIVE MICROFLORA

E. Czerwińska and R. Kowalik

Abstract

Disinfection of contaminated motion picture films and magnetic tapes was carried out in sealed metal cans, having at the bottom and at the lid filter paper discs soaked with 2,5 per cent of 4-chloro-3-cresol dissolved in 96 per cent ethanol.

The contaminated surfaces of audiovisual recordings may be cleaned with well squeezed soft cloth moistened with 4-chloro-3-cresol dissolved in 96 per cent ethanol. The contaminated bobbins may be treated in the same way. Disinfection of air in store-rooms was carried out by using 1 or 2 per cent of 4-chloro-3-cresol in 96 per cent ethanol solution at the amount of 1 g of the microbicide on m³.

In Polish radio and television store-rooms there are many records in the form of motion picture films and magnetic tapes of different origin. Some of them have archival value and we are obliged to preserve them for as long as possible.

Damaging factors

The permanence of audiovisual materials depends among others upon their chemical composition and on protection from dust, harmful fumes and gases. Motion picture films and magnetic tapes are deteriorated by such atmospheric pollutants, as sulphur and nitrogen dioxides, hydrogen sulphide and other substances/3,11,16,23,33,35/. According to Garrell and Calhoun/4/ nitrogen dioxide in reaction with water forms nitric and nitrous acids and these cause serious degradation of sound recording materials. In about 2 hours silver images of black-and-white and colour images on triacetate tape fade severely. Within two days emulsion becomes sticky and after two weeks triacetate tape softens and deforms under the influence of nitrogen dioxide and high moisture content.

Dust and grit act as catalysts in the degrading processes of black-and-white negatives, of colour transparencies, motion picture films and magnetic tapes. This is a well recognized problem/2,3,5,7,10,13,14,18,21,22,27,28,29/. As a result of damages caused by them the playback quality of magnetic tapes becomes worse/2,6,7,11,12,16,23,25,26,32,35,36,37-51/. Dust particles cause not only mechanical damage/emulsion scratching/, but may become also indirect source of chemical and biological degradation. Dust covering on audiovisual

tapes attracts moisture and this minimal amount of water together with gaseous atmospheric pollutants as nitrogen and sulphur dioxides leads to compounds exceedingly dangerous to sound recording materials. Small amounts of water attracted upon tapes by dust constituents are also sufficient to start the growth of fungi, because spores and mycelium fragments are already present on the surface of dust particles. Therefore occasionally even with air conditioning installations fungal problems of sound recording materials may be serious/11,19,26,27,35/.

Conditions of development of fungi depend on the relative humidity of the environment, on the moisture content of material, and also on the temperature, the acidity and the presence of nutrient sources. To initiate the growth of fungi, water sometimes in trace amounts is necessary. Although optimum temperature for fungal metabolism is in general between 24 and 26°C, and optimum for pH lays between 5,0-5,6, some species may vegetate in temperature as low as -7°C and up to +50°C, with pH ranging from 1,0 to 10,0 and relative humidity from 63 per cent.

Fungi requirement as concerns nourishment are very different. Some species may develop on very minimal impurities or, after some period of time, even on hard-decomposing materials. The basic source of nutrient media for fungi and Actinomyces vegetating on audio-

visual tapes are impurities such as dust, fingerprints etc., and also the main emulsion component which is gelatin. In certain cases additional carbon source for fungi may be waxes, used to improve steadiness of the projected image and to protect against friction and fingerprint traces/17/. Although the main synthetic resins with the exception of cellulose nitrate and cellulose acetate are fungi resistant/20,34,35/, fungi and Actinomyces are still able to destroy the plastic in tapes/3,7,16,23,26,27,35,41/. In this case micro-organisms utilize as nutrient source plasticizers, fillers, lubricants and extenders incorporated into magnetic tapes and motion picture films to obtain the necessary physico-chemical properties of these sound recorders.

EXPERIMENTAL PART

The damages caused by fungal activity, as observed in Polish sound recording archives on some motion picture films and magnetic tapes clearly indicated the need for studies on the possibilities of protection of these records against micro-organisms. Considering the character and susceptibility of emulsion upon various agents and the probability that the additives would interfere with photographic and sound properties of the emulsion, the killing of fungi, which develop on motion picture film and magnetic tapes was very com-

pounded. It limits the possibility of the selection of biocide. We were decided to not use for the protection of motion picture films and magnetic tapes the compounds, activity of which depends upon intermediate contact. Therefore utilization of fungicide effective in a vapour form only has been considered. Out of the chemical compounds of this type 4-chloro-3-cresol seemed us the most suitable.

The program of the work in our laboratory was the following:

- Isolation and identification of micro-organisms occurring on sound recordings and in store-rooms
- Tests of microbioresistance of bobbins and sealing tapes
- Search for a method of protection of audiovisual recordings against microbial agents

The isolation of fungi was carried out by three methods:

- by direct streaking of fungi taken out from magnetic tapes or motion picture films on potato-dextrose agar medium/200 g of sliced potato + 1 liter of distilled water + 20 g of glucose and 17 g of agar-agar/.PH was adjusted to 5,5.
- by placing 2 cm long strips of films or tapes contaminated with fungi in Petri dishes, on potato-dextrose agar or on filter paper discs with liquid culture medium of Greathouse, Klemme, Barker of pH=5,5-5,6.

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-by using the method of impressions. In this case sterilized filter paper discs were pressed against spots of microflora, growing on films or on magnetic tapes. These discs with fragments of mycelium or spores were transferred to Petri dishes, and 15 ml of liquid medium of Greathouse, Klemme, Barker of pH=5,5-5,6 was poured into every 100 mm Petri dish.

Microflora which exists in the air of particular air conditioned and not conditioned store-rooms was isolated in the following way:

-Sterilized Petri dishes with filter paper discs were placed at various parts of store-rooms and left open for one hour. After that 15 ml of Greathouse, Klemme, Barker liquid medium was poured into every 100 mm Petri dish.

All dishes with samples were incubated at a temperature of 24-26°C and 90 per cent of relative humidity during a period of three weeks. The developing colonies of fungi were transferred on potato-dextrose agar medium and after obtaining pure cultures the particular micro-organisms were identified.

The microbioresistance of bobbins and sealing tapes

These auxiliary materials also have been tested. Bobbins of different origin/Austrian, English, French, Polish, USA/ were placed in Petri dishes or desiccators in a humid atmosphere. One set of bobbins was contami-

nated with a water suspension of 12 species of fungi spores isolated from motion picture films and magnetic tapes, and the other identical set with a water suspension of spores of *Aspergillus niger*, *Penicillium funiculosum*, *Trichoderma viride* and *Chaetomium glebosum*, as used to test the microbieresistance of synthetic materials, according to International Standard Organization method.

Also 50 mm long fragments of scotch or other sealing tapes were placed in Petri dishes on glass slides in a humid atmosphere and inoculated with fungi spores as previously. The determination of microbieresistance was made after 4 weeks of incubation at a temperature of 24-26°C and 90 per cent of relative humidity.

Methods of disinfection

Disinfection methods for audiovisual recordings have been tested in laboratory experiments and in store-rooms conditions. 4-Chloro-3-cresol at different concentrations has been chosen for the experiments.

In preliminary laboratory experiments the influence of vapour action of 4-chloro-3-cresol on fungi growing in Petri dishes on hardened potato-dextrose agar medium was investigated. The tests were also made on contaminated and not contaminated strips of tapes, which have been subjected in both cases the vapour action of 4-chloro-3-cresol.

The tests were made in test tubes on sloped potato-

dextrose agar medium or in Petri dishes on V shaped glass sticks. In the case of test tubes, loosely fitting cotton wool plugs were put inside the test tubes above hardened medium and on the surface of cotton wool plugs filter paper discs soaked with 4-chloro-3-cresol were placed and the test tubes were tightly closed. In the case of Petri dishes tests, at the bottoms of Petri dishes sterilized distilled water soaked filter paper was placed, and at the lids discs imbibed with fungicide were put in. The Petri dishes were sealed with tape. The evaluation of fungitoxic vapour action was made visually or under the microscope, after 2 weeks culture at a temperature of $24-26^{\circ}\text{C}$.

The tests carried out directly in store-rooms included disinfection of contaminated motion picture films and magnetic tapes placed in sealed metal cans, having at the bottom or both at the bottom and at the lid filter paper discs soaked with ethanol solution of 4-chloro-3-cresol. The contaminated surface of the audiovisual material was cleaned with a well squeezed soft cloth moistened with 4-chloro-3-cresol dissolved in 70 or 96 per cent ethanol. Bobbins and cans were treated in the same way. Also experimental disinfection of air in store-rooms was carried out by using in aerosol spray a 1 per cent or 2 per cent ethanol solution of 4-chloro-3-cresol at the amount of 1 g/m^3 .

RESULTS

It was found that the most often occurring fungi on motion picture films and magnetic tapes were the members of the genus *Aspergillus* and *Penicillium*, beside that *Chaetomium*, *Cladosporium*, *Stemphylium*, *Alternaria* and *Streptomyces*.

Out of the atmosphere of air conditioned storerooms as a rule *Penicillium* and *Aspergillus* have been isolated.

Considering the results of our studies with different concentrations of 4-chloro-3-cresol in test tubes and Petri dishes upon fungi growing on agar media and on contaminated with fungi motion picture films and magnetic tapes it was concluded that filter paper discs imbibed with 2,5 per cent solution of 4-chloro-3-cresol in 96 per cent ethanol inhibited completely the growth of fungi.

After 6 months of storing, no traces of fungal growth was observed on contaminated motion picture films and magnetic tapes, which have been placed in the sealed metal cans, having at the bottom and at the lid filter paper discs soaked 2,5 per cent ethanol solution of 4-chloro-3-cresol.

According to our experiments it is desired however to clean the surface of heavy contaminated tapes or films before placing them in the cans. This treatment may be

made with soft cloth or filter paper, which has been soaked in 2,5 per cent in 96 per cent ethanol solution of 4-chloro-3-cresol, and left until ethanol evaporates.

Not only fungi isolated from audiovisual materials and store-rooms atmosphere develop on the bobbins but also the genres utilized to the evaluation of microbio-resistance of plastics. On the bobbins of Polish, USA /Kodak/ and Austrian origin the most often occurring fungus was *Chaetomium globosum* Kunze. Therefore bobbins should be disinfected too. Good results have been obtained by wiping contaminated bobbins with well squeezed soft cloth moistened with 2,5 per cent in 96 per cent ethanol solution of 4-chloro-3-cresol.

It was observed that disinfection of air conditioned store-rooms with aerosol of 1 per cent ethanol solution of 4-chloro-3-cresol at the amount of 1 g/m^3 is sufficient, whereas in heavily dusted store-rooms even a 2 per cent solution of 4-chloro-3-cresol was not sufficient. The most fungicide resistant fungi were: *Aspergillus terreus* Link and sometimes *Chaetomium globosum* Kunze.

We wish to thank doc. dr. Hanna Jędrzejewska for a necessary revision of this manuscript, the assistant director for preservation, The Library of Congress, Mr. Frazer G. Poole, who so promptly supplied us with the difficult to obtain reprints and booklets, and Mr. Elmer A. Barthold from Rohm and Haas, Philadelphia, for kindly sending the sample of Hyamine 1622 for the tests.

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LA CONSERVATION DES PHOTOTYPES
GELATINO-ARGENTIQUES NOIR ET BLANC
SUR SUPPORT TRI-ACETATE DE CELLULOSE
ET POLYESTER

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5ème Réunion triennale
Zagreb, 1978

LA CONSERVATION DES PHOTOTYPES GELATINO-ARGENTIQUES
NOIR ET BLANC SUR SUPPORT TRI-ACETATE DE CELLULOSE
ET POLYESTER

Martine Gillet et Françoise Flieder

La conservation des documents photographiques et cinématographiques est un problème qui devient de plus en plus urgent à résoudre et sur lequel le *Centre de Recherches sur la Conservation des Documents Graphiques* a dû se pencher afin de pouvoir conseiller les responsables d'archives. Devant la nature très variée des documents à conserver (daguerréotypes, ambrotypes, ferrotypes, calotypes, surfaces gélantino-argentiques, thermocopies, électrocopies, procédés vésiculaires et diazoïques), il nous a fallu choisir l'objet des premières recherches. En fonction des différentes demandes, nous avons commencé l'étude par les surfaces gélantino-argentiques noir et blanc sur support tri-acétate de cellulose et polyester.

Malgré l'abondance des données de la littérature concernant ce sujet (1-33), nous avons voulu cependant approfondir certains points qui nous paraissaient de première importance. Dans ce présent rapport, nous avons fait une synthèse des travaux déjà publiés auxquels nous joignons les résultats de nos propres expériences.

Nous avons classé l'ensemble des données bibliographiques selon trois grands thèmes : *influence des produits chimiques résiduels, influence de l'environnement, choix des contenants.*

1. EXPOSE DES TRAVAUX ANTERIEURS

1.1. Influence des produits chimiques résiduels (34 à 67)

Une des premières conditions pour qu'un film développé se conserve sans altération, est que ce film soit exempt de tous produits chimiques résiduels provenant des bains de développement. Lorsque le traitement du film a été bien effectué, la teneur en produits chimiques résiduels est pratiquement nulle. Le lavage du film est donc une phase très importante pour la conservation. En effet, le thiosulfate de sodium ou d'ammonium utilisé pour le fixage et restant sur l'image du film, se décompose très rapidement pour donner des sulfures, des polythionates et de l'acide sulfurique.

Ces produits de décomposition occasionnent un jaunissement et un pâlissement de l'image. L'action du thiosulfate se manifeste principalement dans les demi-teintes et les noirs de l'image, tandis que celle de ses dérivés est surtout visible dans les blancs où elle apporte une densité colorée supplémentaire.

Plusieurs normes concernant la conservation d'archives des phototypes fixent le taux maximal en thiosulfate résiduel à $0,7 \mu\text{g}/\text{cm}^2$.

Pour un archivage de longue durée, il est donc nécessaire de vérifier que les films ou papiers photographiques sont conformes aux normes du point de vue de la teneur en produits chimiques résiduels, sinon il faudra procéder au relavage des documents. De nombreuses méthodes de détermination de cette teneur sont décrites dans la lit-

térature. Dès 1930, J.I. CRABTREE et J.F. ROSS (43) ont mis au point un test dans lequel le thiosulfate extrait d'un échantillon de film réagit avec du bromure mercurique pour donner un précipité. La turbidité formée est mesurée par comparaison avec des étalons connus. Cette méthode était recommandée par l'American Standards Association (35). Mais étant donné son manque de sensibilité, C.D. WARBURTON et E.P. PRZYBYLOWICZ (66) ont décrit un test sept fois plus sensible, basé sur la réduction du thiosulfate en sulfure par le borohydrure de sodium. Ce sulfure réagit avec la N,N-diméthyl-p-phénylènediamine pour former du bleu de méthylène, lequel est dosé par absorption dans l'ultra-violet. Or, la stabilité du thiosulfate est éphémère : après 24 heures, il se décompose et les produits de décomposition n'étant pas dosés par cette méthode, il est nécessaire de faire la mesure rapidement après le développement.

Une autre méthode mise au point par J.I. CRABTREE, G.I. EATON et L.E. MUEHLER (41), reprise et modifiée par D.A. MATTEY et R.W. HENN (48), permet de déterminer à la fois les quantités de thiosulfate et de thionates : ces derniers composés réagissent avec du nitrate d'argent pour donner du sulfure d'argent. La densité résultante est lue sur un densitomètre. La méthode au bleu de méthylène et la méthode au nitrate d'argent sont normalisées par l'American Standard Institute (51) et applicables à tout type de films, plaques et papiers, noir et blanc ou couleur.

1.2. Influence de l'environnement (68 à 85)

1.2.1. *La température et l'humidité*

Tous les auteurs sont unanimes pour dénoncer l'influence néfaste de la chaleur et de l'humidité sur la conservation des surfaces gélantino-argentiques noir et blanc. L'émulsion subit des détériorations avant que le support (en triacétate de cellulose ou en polyester) ne soit atteint.

Une humidité relative supérieure à 50-60 % accélère la perte des contrastes, augmente le retrait, cause le ramollissement de la gélatine et favorise la croissance des champignons. Par contre, une humidité relative basse augmente la susceptibilité du film aux effets statiques, aux craquelures et au "curl".

Quand la température croît, le retrait et la distorsion augmentent, la résistance à la traction du film diminue.

De plus, des variations brutales de température et d'humidité sont les facteurs les plus à craindre pour les documents à conserver. P.Z. ADELSTEIN et J.L. MAC CREA (68) ont obtenu une craquelure de la gélatine sur un film Estar (polyester) en faisant des cycles d'humidité allant de 10-20 % d'humidité relative à 60-70 % H.R. à 21°C. Il faut donc essayer de maintenir des conditions climatiques les plus stables possibles. En cas de changement d'atmosphère, les documents devront être préconditionnés.

La durée nécessaire à l'équilibrage à 100 % varie suivant le type de document : 90 mn pour une bande simple ou une fiche, 3 semaines pour un rouleau de 16 mm, et 4 semaines pour un rouleau de 35 mm.

Les phototypes doivent être conservés dans des locaux climatisés suivant une spécification très bien déterminée.

Plusieurs installations de la sorte sont réalisées dans divers pays : le Centre des Archives du Film à Bois d'Arcy en France (83), The British National Film Archive (74) et les Archives du Film de la République Démocratique allemande à Berlin (85) conservent les films à $12^{\circ}\text{C} + 2^{\circ}\text{C}$ et 50 % + 10 % d'humidité relative. Tous les auteurs prescrivent une humidité relative inférieure à 60 %, voire à 50 % et une température inférieure à 20°C .

Plusieurs normes ont été établies afin de préciser les conditions climatiques suivant les types de matériau. Les dernières établies prescrivent une température inférieure à 21°C pour une humidité relative comprise entre 15 et 50 %. La limite inférieure d'humidité relative est ramenée à 30 % dans le cas des microfilms.

Lorsque dans une même réserve on doit conserver des films de nature différente (nitrate, etc...), il est recommandé de maintenir l'humidité relative à 30 %.

1.2.2. *La pollution*

La pollution atmosphérique est également un facteur à contrôler.

En effet, tous gaz ou produits chimiques oxydants contenus dans l'atmosphère attaquent irrémédiablement les phototypes gélatino-argentiques. Les composés soufrés (tels que le sulfure d'hydrogène ou le dioxyde de soufre) causent une détérioration lente du support du film et de la gélatine, en même temps qu'un pâlisement de l'image.

Les oxydes d'azote provenant de la décomposition des supports de films en nitrate de cellulose (libération d'acides nitreux et nitrique, en présence d'humidité), sont des agents oxydants qui décolorent l'image, dégradent la gélatine et enfin décomposent le support en acétate de cellulose.

Les dommages occasionnés par ces composés oxydants sur les images des microfilms sont matérialisés par des taches d'oxydo-réduction : il y a oxydation locale de l'argent de l'image causant ainsi la formation de dépôts minuscules d'argent colloïdal coloré (brun jaunâtre, taches de 10 à $15\ \mu$ de diamètre). L'étendue des taches augmente de 50 % en 5 ans.

Tous les peroxydes sont également à proscrire étant donné leur pouvoir oxydant élevé. Ils produisent le même effet, c'est-à-dire des taches brunes sur l'image.

Des expériences américaines ont montré que la pollution atmosphérique ayant détérioré des microfilms n'atteignait pas 10^{-7} à 10^{-9} mole/l. Il est donc très difficile de contrôler la pollution. Il faut cependant purifier l'air des enceintes de stockage des matériaux photo-sensibles, de tous les agents polluants décrits précédemment, y compris la poussière.

Il existe une méthode pour tester les atmosphères des locaux d'archivage : elle utilise des couches d'argent colloïdal jaune qui se décolore fortement en présence d'agents oxydants.

1.2.3. *Les microorganismes*

La gélatine des phototypes est un excellent milieu de culture pour les champignons et les bactéries dont la croissance sera d'autant plus favorisée que l'humidité sera plus forte.

Ces microorganismes, pour se développer, doivent puiser le carbone qui leur est nécessaire dans la gélatine dont ils modifient la composition chimique. Cette transformation entraîne irrémédiablement une modification physique se traduisant de différentes manières : aspect plus ou moins "poisseux" allant même jusqu'à la liquéfaction ; détachement de la gélatine de son support.

1.3. *Choix des contenants (86-87)*

Vu la nocivité de nombreux produits oxydants vis-à-vis des phototypes, les contenants, c'est-à-dire les pochettes et les boîtes, ne doivent ni dégager de composés corrosifs, ni être hygroscopiques. Il est donc conseillé d'utiliser des matériaux tels que l'aluminium anodisé, l'acier inoxydable et les plastiques libres de peroxydes.

L'emploi du plexiglas est très contesté. E. OSTROFF (17) affirme son inertie vis-à-vis des matériaux photographiques. Par contre, la Société KODAK à Rochester a effectué des essais qui tendaient à prouver son action nocive.

Tous les papiers et cartons constitués de pâte mécanique ne comprenant pas de purification doivent être éliminés ; ils contiennent de la lignine qui est dégradée par la chaleur et la lumière en acides organiques (ex. : le papier kraft). Pour les papiers exempts de tout élément oxydant, le pH doit être neutre ou légèrement supérieur à 7. A la *Library of Congress* de Washington, ils utilisent un papier neutre *Permalife paper*.

Lorsque l'on ne dispose pas de locaux climatisés, il est conseillé de stocker les archives dans des contenants scellés où l'on a créé un "micro-climat", c'est-à-dire une humidité relative inférieure à 30 %. L'Institut national suédois d'essai des matériaux préconise deux types de pochettes pour microfilms d'archives : l'une est constituée par plusieurs couches successives de : polyester - aluminium - polyester - polyéthylène ; l'autre est une pochette en polypropylène scellée dans une boîte d'aluminium également scellée. G.T. EATON (8) propose lui aussi un complexe aluminium-polyéthylène pour envelopper les photographies.

Le problème des adhésifs et du vernis pour meubles de rangement à utiliser est le même que celui des contenants : ils ne doivent pas contenir d'impuretés (peroxydes, fer, cuivre ou soufre) et ne pas être hygroscopiques.

Il existe un test simple qui permet de vérifier que les matériaux employés pour la conservation des documents photographiques sont exempts d'impuretés chimiques (86) : une plaque d'argent en contact 2 fois 8 heures à 75°C avec le matériau à tester ne doit pas être ternie.

2. RESULTATS EXPERIMENTAUX

De très nombreuses expériences ont été réalisées au laboratoire depuis deux ans. Ne pouvant donner ici l'exposé détaillé de nos recherches, nous nous limiterons à ne présenter que les travaux ayant abouti à des réalisations pratiques.

2.1. Dosage des produits chimiques résiduels

Nous avons expérimenté les différentes méthodes de mesure du thiosulfate résiduel et de ses produits de décomposition.

Trois méthodes peuvent être utilisées, chacune d'elles ayant cependant une application bien déterminée :

La méthode dite "*au nitrate d'argent*" (48) est appliquée aisément pour la mesure du thiosulfate résiduel et de ses produits de décomposition dans les films et les papiers. Elle est peu précise et présente un caractère limitatif car le dosage doit être effectué sur des images de densité assez faible (de 0,2 à 1 maximum). En effet, le sulfure d'argent formé augmente la densité de l'image : afin que cette mesure soit précise, le contraste doit être grand. Sur les plages de densité élevée, le contraste risquerait d'être nul.

La méthode dite "*au chlorure mercurique*" (50) est une technique rapide mais également peu précise que nous employons lorsque l'on désire simplement savoir si les documents ont été bien lavés, c'est-à-dire si la teneur en thiosulfate est inférieure à la limite admise.

Lorsque cette teneur en thiosulfate doit être connue plus précisément, par exemple pour des documents de grande valeur, il est préférable d'utiliser la méthode dite "*au bleu de méthylène*".

La méthode dite "*au bleu de méthylène*", décrite par C.D. WARBURTON et E.P. PRZYBYLOWICZ (66) et normalisée par l'American National Standard Institute (51) a fait l'objet d'une mise au point dans notre laboratoire. Il est conseillé d'utiliser le borohydrure de potassium (au lieu du borohydrure de sodium), le sulfate de la para-diméthyl-phénylène-diamine et de conserver tous les réactifs à 4°C. Tous les produits doivent être renouvelés régulièrement (tous les 4 ou 5 mois). Ainsi nous avons obtenu des résultats satisfaisants qui nous permettent d'utiliser couramment cette méthode.

Une quatrième méthode décrite par J. POURADIER et H. CHATEAU (60) sert à doser tous les produits de décomposition du thiosulfate pouvant s'être formés sur les phototypes anciens. Nous avons longuement expérimenté ce dosage sans succès et l'avons donc abandonné.

2.2. Etude d'un procédé de désinfection

Les champignons que nous avons isolés sur les phototypes constituent une flore très importante. Les espèces recensées se répartissent dans les deux grandes classes :

- les Ascomycètes, dont les formes les plus fréquentes sont les *Chaetomium* ;
- les Adelomycètes (*Fungi imperfecti*), plus spécialement représentés par des *Penicillium*, *Aspergillus* et *Fusarium*.

Quelques bactéries se sont également développées sur la gélatine mais leur nombre est cependant très réduit.

Avant de choisir une technique de désinfection, il faut toujours s'assurer, non seulement de l'efficacité des produits utilisés, mais également de leur innocuité vis-à-vis des constituants, car un très grand nombre d'entre eux sont toxiques pour le personnel et peuvent nuire à la densité de l'image et à sa définition. Une des grandes difficultés pour la désinfection des documents résulte de la pénétration profonde des champignons au coeur des piles de photographies et des bobines de films. C'est ce qui explique qu'aucun traitement de surface n'est suffisant dans ce cas particulier, et c'est également ce qui justifie la préférence donnée aux procédés de désinfection en autoclave sous vide, grâce auxquels les gaz désinfectants pénètrent dans toutes les cavités des documents contaminés.

Parmi les nombreux traitements qui ont été expérimentés, seul l'oxyde d'éthylène (9) a donné de bons résultats pour la désinfection. L'opération s'effectue dans un autoclave dans lequel on crée un vide suffisant pour obtenir une pression comprise entre 10 et 60 mm de mercure. On introduit alors simultanément l'oxyde d'éthylène et l'air, en proportions déterminées (27,5 % de gaz et 72,5 % d'air), afin de rétablir à l'intérieur de l'autoclave une pression très légèrement inférieure à la pression atmosphérique ambiante, cela pour éviter toute possibilité de diffusion du mélange vers l'extérieur. La quantité d'oxyde d'éthylène utilisée est de 500 g/m³. Le traitement est réalisé à 20°C et dure 6 heures (c'est entre 20° et 22°C que l'oxyde d'éthylène atteint son maximum d'efficacité).

Afin de vérifier la résistance physico-chimique d'un film ainsi traité, nous avons choisi un certain nombre de tests. Parmi eux (résistance à la traction, à la déchirure amorcée, à l'éclatement, aux doubles plis, fluage, retrait, acidité, viscosité du support et densité optique de l'image), seules la mesure du retrait du film et la modification de la densité optique de l'image nous ont donné des résultats significatifs d'une altération. Nous les avons donc retenus. Tous les essais ont été réalisés sur une pellicule Kodak 5234 DN GF*. Afin de connaître le comportement dans le temps des documents ainsi traités, les analyses ont été faites après vieillissement artificiel (4 h. pour l'un et 8 h. pour l'autre à 48° et 95 % H.R.) (voir tableau).

Dans tous les cas, on observe que le retrait est nul et que la densité optique reste inchangée. Ces résultats satisfaisants ont été également vérifiés sur de vieux films.

Nous pensons donc que l'oxyde d'éthylène est tout indiqué pour la désinfection des phototypes noir et blanc.

* Film gélatino-argentique noir et blanc sur support en triacétate de cellulose, exposé en machine continue Debie, à 100 m/h et 2850° Kelvin, puis développé dans un bain négatif D 76 noir et blanc.

CONCLUSION

Notre étude bibliographique nous a permis de mettre en évidence les différents facteurs qui interviennent dans la détérioration des phototypes noir et blanc : la teneur en produits chimiques résiduels, les contaminations biologiques, la température, l'humidité ainsi que la pollution atmosphérique.

Parmi les travaux expérimentaux réalisés au laboratoire, certains nous permettent de formuler, dès à présent, des conseils aux responsables d'archives photographiques et cinématographiques.

Le dosage des produits chimiques résiduels est applicable quels que soient les besoins : la teneur en thiosulfate peut être mesurée rapidement pour le simple contrôle du lavage, et de manière plus précise sur des phototypes fraîchement développés ou sur des fonds anciens destinés à un archivage de longue durée.

Il est recommandé de désinfecter tout document contaminé par les microorganismes avant le stockage dans des locaux, afin d'éviter la propagation des spores. A cet effet, nous préconisons une méthode expérimentée au laboratoire, utilisant l'oxyde d'éthylène qui détruit tous les microorganismes sans aucun dommage pour les films, microfilms sur support triacétate de cellulose.

Des études ayant trait, d'une part à l'influence de l'environnement, d'autre part au choix des contenants à utiliser pour un archivage de longue durée sont en cours de réalisation. Les premiers résultats obtenus sur une même pellicule sont intéressants. Mais avant de tirer des conclusions définitives, il est nécessaire de renouveler les expériences sur des films de nature très variée.

Parallèlement, nous entreprendrons des recherches sur les techniques de restauration des photographies anciennes.

RESUME

De nombreux facteurs d'altération des phototypes gélatino-argentiques noir et blanc ont été mis en évidence et largement décrits dans la littérature. Le thiosulfate résiduel, utilisé pour le fixage et restant après traitement, génère, en se décomposant, des sulfures, polythionates et acide sulfurique qui jaunissent et pâlisent l'image ; pour le doser, il existe plusieurs procédés dont nous avons retenu, après expérimentation, les mieux adaptés et les plus précis.

Une méthode de désinfection à l'oxyde d'éthylène des phototypes contaminés par les microorganismes, a été mise au point dans notre laboratoire ; elle arrête la prolifération microbiologique sans endommager le document.

L'influence néfaste de la température, de l'humidité et de la pollution a été démontrée, par de nombreux auteurs qui préconisent, pour un archivage de longue durée des phototypes, l'installation de réserves climatisées et l'utilisation de contenants exempts de tous agents polluants.

INFLUENCE DE L'OXYDE D'ETHYLENE
sur les films gélatino-argentiques noir et blanc
(support en tri-acétate de cellulose)

Référence :	Traitement	Retrait :	Densité
A ₀	témoin	4,747	1,90
A ₄ (= A ₂)	6 heures oxyde d'éthylène (500 g/m ³)	4,747	1,91
A ₁₈	4 heures à 48° et 95 % H.R.	4,736	1,92
A ₂₅	4 heures à 48° et 95 % H.R. + 6 heures oxyde d'éthylène (500 g/m ³)	4,737	1,94
A ₁₇	8 heures à 48° et 95 % H.R.	4,733	1,94
A ₂₆	8 heures à 48° et 95 % H.R. + 6 heures oxyde d'éthylène (500 g/m ³)	4,733	1,95

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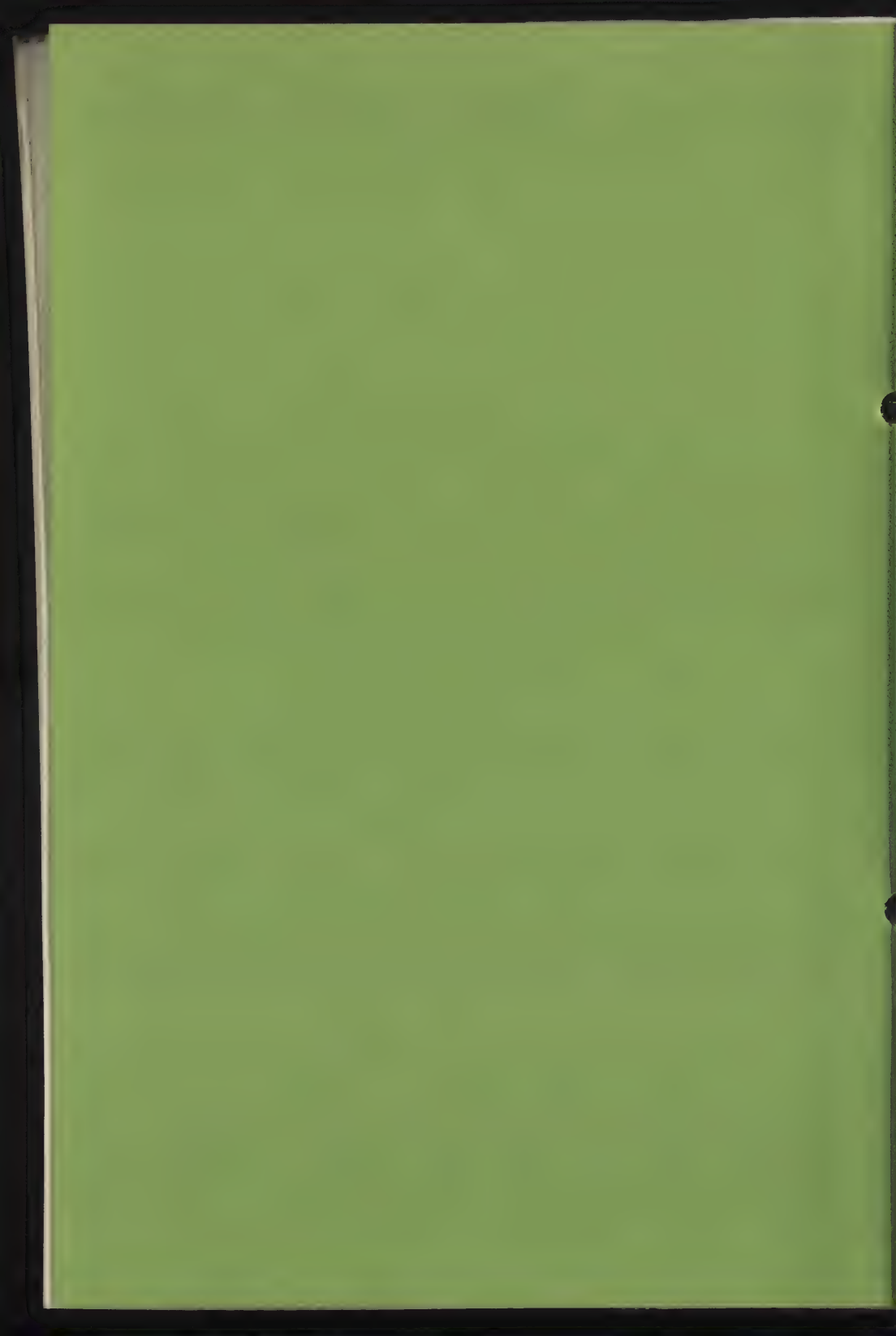
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CONSERVATION AND RESTORATION OF BIRCH-
BARK MANUSCRIPTS

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CONSERVATION AND RESTORATION OF BIRCH-BARK MANUSCRIPTS

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There is quite a number of documents inscribed on birch bark that have been preserved in museums and archives up to the present time. Birch bark was used as writing materials in the far past. A good number of single bark manuscripts are known as well as whole books are kept in repositories.

Birch bark manuscripts found in Novgorod are unique monuments of Russian literary culture.

A whole library of birch bark manuscripts has been formed during the recent decades.

The problem of preserving these objects of historic value is one of the essential problems of restoration and conservation.

Birch bark is preserved in two cases - when there is no air or moisture access to it. Humidity is very high in Novgorod and other Russian towns with their cultural layer preserving birch bark fairly well. The layer there is fully saturated with ground waters found no deeper than 1.5-2 metres below ground level cutting air access to all the ancient objects lying beneath. Covered up with earth, birch bark has for centuries suffered an unceasing effect of constantly flowing water.

Birch bark manuscripts are, as a rule, not merely pieces of birch bark with inscriptions on them. A special process of preparing birch bark for writing preceded. Bark was peeled off an unguarled part of a birch of medium thickness growing on solid, rising ground.

Birch bark, i.e. the outer covering layer of birch bark, is known to consist of many tightly clinging together but easily separated thin layers varying in colour. These layers are separated and the thinnest, for the most part inner plates are chosen.

The chosen bark is still rough and lacks sufficient softness; it should be "boiled thoroughly". Birch bark heated in hot water for an hour is ready to be used.

For eighteenth century manuscripts only the top and very thin layer was used while rather thick multi-layer pieces were commonly used for ancient Novgorodian manuscripts.

Manuscripts are found in the form of scrolls.

Examination of letters makes it possible to ascertain that they were marked on bark by tools made of bone.

Letters of the manuscripts' text were scratched or more exactly pressed out over the surface of birch bark with some sharp instrument. A great number of tools for writing-scratching on birch bark have been found, made of bone, metal, to include even wood shanks having a sharp point at one end and a shovel-like point at the other with a hole in it to hang a stylus on a girdle.

Such "styles" leave marks on modern birch bark which are similar to those forming letters engraved on ancient manuscripts.

Capability of being scratched turned to be the major property contributing to preservation of manuscripts' texts from destruction for ages to come.

As a rule, letters are engraved on the inner, smoother surface of birch bark. When a sheet of bark is wound upon itself into a roll its inner surface

becomes the outer side. Birch bark for manuscripts served its purpose in its full thickness.

In Russia, birch bark was a cheap and easily available material used in building for making, kitchen utensils and household objects as well as for writing. The first birch bark manuscripts date back as far as the ninth century. Texts ingraved on them with a bone or metal stick - a "scratcher", have hitherto succeeded to maintain a sufficient appearance of relief, thus witnessing the fact that our ancestors successfully used natural qualities of the material.

Distruction and conservation

Birch bark consists of a great number of layers every one of them being very thin.

Its destruction process goes in two ways:

- (1) separation of layers from each other;
- (2) destruction of the layer itself, cracking of layers.

Birch bark with its layers scaled is very hard to restore, mainly for its knots preventing the adhesive to be evenly covered on all the sheet's segments even with a thin brush.

The risk of cracks likely to appear around the knots is always present.

Birch bark becomes very brittle eventually. The sheet turns very rigid and frail and, then, gradually disintegrates. A birch bark manuscript should not be spread open right after its discovery. In this case it might be broken even by slight bending. It is to be heated in hot water and washed with a brush ever so gently. Stress of layers is reduced at a high temperature only.

A washed manuscript is then carefully scaled. Layer separation is necessitated by the need of conserving manuscripts' text. Non-uniform drying of inner and outer layers leads to longitudinal and transverse birch bark cracking fraught with destruction of text.

Therefore, to avoid loss of text layer separation is applied.

Birch bark is actually a protective covering on the birch trunk. But in spite of the material's strength cases of destruction of birch bark have been registered.

Methods of conservation practised in respect of archaeological wood proved to be absolutely unacceptable when tried on birch bark.

Examination of micro-cross sections of birch bark, its physical and chemical properties helped to determine correctly the reasons for and nature of destruction of birch bark manuscripts. Destruction of any archaeological material should be related with conditions of its lying in earth. It is quite natural that birch bark is to suffer a number of changes while staying in soil for thousands of years.

Only having studied these problems, that is structural changes, physico-chemical properties, effects of soil conditions, is it possible to approach birch bark conservation problem-solving. It was found as a result of anatomical and chemical analyses of birch bark that suberene content both in new and archaeological birch bark is nearly identical varying within the limits of 20 to 35 per cent.

Suberene in birch bark is chemically bonded with other ingredients and can be extracted only by way of high-temperature heating under certain conditions. Birch bark suberene is a thermoplastic substance with a high content of saturated oxyacids.

Birch bark is a cork layer on the outside of birch bark proper.

Cork layer cells are rectangular on a transverse incision and multangular on a tangential one. They are closely connected with each other and there are no intercellular spaces between them. Cork cell membranes have no pores and are saturated with suberene to make it water- and airtight.

In most cases, there are specific small fragments of friable texture, known as lenticels to serve as ventilating channels on the outside of cork tissue. Birch lenticels look like narrow cross strips.

A birch bark conservation method has been elaborated on the basis of results obtained in the course of experimental investigations after scrutinizing technological techniques of ancient birch bark treatment. Temperature conditions of treatment as well as salt removal process are a major factor of birch bark conservation.

Birch bark is washed in hot distilled water to be changed repeatedly as it gets dirty and cools down. The temperature should not be lower than 75-80°C. A higher temperature is one of the pacing conditions for birch bark treatment.

Birch bark having spent many centuries in soil suffered changes of some sort. Cork cells consolidated still more.

Side plates spread out and the roll streightens under the influence of high temperature.

Investigations of archaeological birch bark have noted that content of water-soluble salts (Ca, Na, Mg) is much higher than that of newly prepared birch bark. It is, evidently, the result of soil salting. This is why birch bark washing in distilled water is most essential.

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Birch bark cracking was frequently observed as a result of manuscript storage. A large content of water-soluble salts in ancient birch bark is also likely to be the cause.

Prior to further birch bark conservation it should be disinfected. As it was demonstrated by tests, one per cent water solution of sodium pentachlorophenolate is the most agreeable. An antiseptic is added during the last washing operation.

Washed birch bark may be tested by lean gas doubling, if need be.

In case of evident layer separation, surface strengthening is possible by methylol-polyamide glue PF-2/1. Drawn out from soil, birch bark is placed in conditions completely alien to it. Birch bark keeping is one of major problems. It is put in a passe-partout pressed between two glasses. The glasses are framed with a neutral adhesive tape. In this form birch bark manuscripts have already been kept on shelves for decades.

A METHOD OF PREPARING AND USING AN
ACRYLIC RESIN COATED PAPER

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5th Triennial Meeting
Zagreb, 1978



A METHOD OF PREPARING AND USING AN ACRYLIC RESIN COATED PAPER.

Antonio Zappala and Paolo La Mendola

Abstract

This article describes a laboratory apparatus that automatically and continuously impregnates Japanese paper with a suitable resin. The treated paper is then used in bonding fragile documents which could not otherwise be restored.

The bonding is reversible, even after artificial aging, through simple immersion in acetone or other solvents.

At the same time, the bonded document can be immersed, without risk of fragment loss, in aqueous solutions for operations such as washing and deacidification that would be impossible to perform without the bonding.

In addition, a description is given of the operative technique used in dry bonding and the restoration of thin or thick documents.

PART I

APPARATUS FOR AUTOMATIC IMPREGNATION OF PAPER

Introduction

A problem which the restorer of ancient bibliographic material must often face is the need to reinforce paper documents that have become extremely fragile. Such fragility is due to oxidative and hydrolytic deterioration processes affecting the fibrous material of the paper. Moreover, the mechanical resistance of the documents is also notably diminished by wear and micro-organism attack. In such cases the paper becomes so fragile that even simply brushing the surface with a reinforcing solution can be difficult.

In order to solve these problems, the idea of using various techniques for dry bonding of the fragile sheet of paper to another, stable and durable sheet has long been considered. This is intended to restore the document's lost resistance.

The various systems used to date are well known: for instance, lamination with sheets of synthetic material (1-2-3)

or reinforcing paper pre-treated with vinyl or acrylic resins (1-4), or else impregnation of the fragile paper with synthetic polymers (4-5).

The disadvantages of such systems derive, in some cases, from the excessive temperature needed for the operation or, in others, from the low reversibility of the method or the damage the document may suffer due to the solvent employed (5-6).

Choice of materials for dry bonding

To avoid the drawbacks of various bonding systems -- mainly due to the fact that one has to use industrial materials produced for other purposes -- we thought of constructing a laboratory device to impregnate paper automatically for dry bonding. With this, it becomes easier to choose a thermo-fusible adhesive from among the many synthetic resins industrially produced for numerous other uses. Obviously, one can also choose the best type of paper. There are synthetic papers produced today with merit consideration for use in restoration.

To try out the apparatus, which will be described below, we decided to impregnate the Japanese paper normally used in our institute for wet bonding. This paper presents a good transparency, its substance amounts to $11,8 \text{ gr/m}^2$ and its viscosimetric degree of polymerization is high enough and maintains almost the same DPv even after 4 days aging treatment at 105°C (that is DPv=1580 and DPvi=1325 respectively). This type of paper has been used for many years in almost every Italian restoration laboratory.

In choosing an adhesive for the impregnation, we looked for one that had the highest number of the requisite properties listed below. Many authors hold that these characteristics are indispensable for dry bonding (7-1).

The paper and adhesive must:

- 1) - be stable. For example, demonstrate high resistance to deterioration when exposed to normal, expected atmospheric conditions;
- 2) - be flexible and resistant to abrasion, so that they can withstand normal use of the document;
- 3) - bestow a considerable increase in the mechanical resistance of the document being protected; at the same time the bonding should be as thin as possible;
- 4) - not interfere with the document's legibility;
- 5) - not contain additives which could migrate and damage the document;
- 6) - permit bonding to be done with a minimum of effort;

7) - permit removal of the film, if necessary, with a simple method which does not damage the document.

The synthetic resin that seemed most adapted to our requirements is Paraloid B72, an acrylic resin, copolymer of methylacrylate and ethylmethacrylate. In the field of painting restoration this has been used without significant drawbacks for several decades as a protective coating for painting surfaces.

The most outstanding characteristics of this resin are its resistance to aging and its solubility in a large number of solvents (8-9). Even when exposed to severe climatic conditions, it does not yellow, nor does it exhibit the phenomenon of cross-linking which, over a period of time, makes many synthetic resins harder, more brittle, and less soluble. Moreover, this resin exhibits good resistance to temperature increases (8-10-11-12-13) and is effective in protecting the paper during treatment with oxidants; yet it does not react --either to protect or damage -- when the paper is artificially aged at 95°C for 12 days (9). Finally, this polymer is particularly desirable as a thermofusible adhesive because it is absolutely non-adhesive at room temperature (its T_g is 40°C), so that there is no risk that documents bonded with this adhesive and piled together might stick to each other, even under pressure. Furthermore, at a relatively low temperature of about 70°C it is in a semi-fused state so that, penetrating into the pores of the surface of the document being treated, it allows for good anchorage of the reinforcing paper to the document itself. It is difficult to imagine lowering this temperature any further -- for instance by using an adhesive with a lower fusion temperature -- because in this case the T_g would also be lower and there would be a risk of the bonded sheets sticking together.

Description of the apparatus for impregnating Japanese paper

The apparatus was designed to impregnate rolls of Japanese paper continuously and automatically with a suitable resin. The rolls are used just as they come from the supplier; after the paper passes through the apparatus and is impregnated with resin, it is automatically rewound onto another cylinder. The roll of treated paper is removed from the machine and can be kept for long periods until needed for dry bonding fragile documents.

The apparatus is basically composed of two cylinders (A and B in the figure), a tank (C), a small, direct cur-

rent electric motor (D), seven rollers (E), and a rectifier to supply the direct current required by the electric motor. The various parts are supported by a frame, measuring 80 x 80 x 63 cm. The rectifier is simply a car battery charger plugged into the main power supply; its exit tension varies from six to twelve volts. Thus it is possible, by varying within certain limits the current supplied to the motor, to vary the rotation speed of its axle so that it lies between 25 and 70 rpm. The motor is the kind used for ship models and functions on six volts, DC; it can develop a free-running rotation speed of 9,000 rpm, consuming 900 mA when unloaded and up to a maximum of 7,000 when loaded. The rotation speed of the axle can be mechanically reduced through a series of gears down to 25 rpm. This rotation speed is further reduced to 1.66 rpm with a fitting, clearly visible in the photograph, normally used for opening and closing venetian blinds. This device, composed of gears, transfers the rotation of the drive shaft to the roll on which the impregnated paper is wound (B). As cylinder B rotates, it unwinds the paper from cylinder A. As the paper unrolls, it must pass into the tank beneath a metal roller which turns freely on bearings (see fig.2, detail 1) but which cannot be raised because it is held in place by two metal strips cut to fit (fig.2). These strips are fixed in place by two wing nuts, one of which can be seen in photo 2. After passing into the tank, the paper --now impregnated with the solution of Paraloid in ethylene tetrachloride -- skims the upper edge of the tank in such a way that the excess solution is automatically removed and returns to the tank. The paper is obviously wet as it leaves the tank; the ethylene tetrachloride must be allowed to evaporate completely before the paper is rewound -- otherwise the paper roll might become glued together. To facilitate evaporation the impregnated paper is made to travel some distance, passing over the first upper roller, then beneath the first lower roller, then over the next upper one, and so on until it is wound onto cylinder B. Obviously the distance and the speed at which it moves, are calculated so that the paper itself stays free long enough for the solvent to evaporate completely. In practice, we have found this takes about five minutes; it can obviously vary considerably, depending on the ambient temperature and, above all, on the ventilation to which the entire apparatus is exposed. Both to increase the ventilation and principally to protect the operator from breathing solvent fumes during the impregnation, the apparatus

is put under an exhaust hood of the sort used in chemical laboratories. With this it is possible to expell the tetra-chloroethilene fumes as they develop. Since the rotation speed of the winding cylinder is 1.66 rpm and its circumference is 26 cm, the paper travels a distance of circa 44 cm per minute. The number of "E" rollers, and the distance between them, is such that the total route before rewinding on cylinder B is 320 cm long. At the speed give above, it takes about seven minutes to cover this distance; this time is longer than necessary for complete evaporation of the solvent. The seven rollers shown in the drawings and photographs are glass tubes 25 mm in diameter and 70 cm long, closed at the ends with pierced rubber plugs, as shown in details 1 and 2 of fig.1. An iron rod, 6 mm in diameter passes through the holes in the plugs and extends from the two ends of the glass tube; two bearings are fixed on the rod and rest on two grooves attached to the framework. In this way the rollers are free to turn with almost no friction. The upper rollers can be raised and removed from the apparatus for easier cleaning; the lower ones, instead, are fixed in place and the screws holding the bearings must be undone in order to dismantle them. The roller inside the tank (fig.2) below the liquid level is made of brass and sealed at the ends with two cylinders of soldered brass. In constructing this roller it is clearly not possible to use rubber plugs which would partially dissolved in the solvent. This roller, which is 25 mm in diameter and 70 cm long, also bears at each end, like the glass rollers, two iron rods, 6 mm in diameter, with two bearings attached.

Procedures for using the apparatus

To use the apparatus the first step is to place the roll of Japanese paper, as it comes from the supplier, in the position of cylinder A. Check to see that the roll can turn freely with light friction. If Japanese paper is available only in sheets, one must prepare a roll by gluing the sheets in succession with an adhesive which is not soluble in tetrachloroethylene. Starch paste can be used in such a situation. It is important to align the various sheets perfectly. After arranging the roll, the end of hte paper must be passed under the roller in the tank. To facilitate this operation, it is advisable to take the roller out of the tank after removing the fasteners which hold it in place. Then replace the metal roller; check that it turns freely on its bearings and that is well fastened down so that it cannot be lifted by the tension of the paper when the ap-

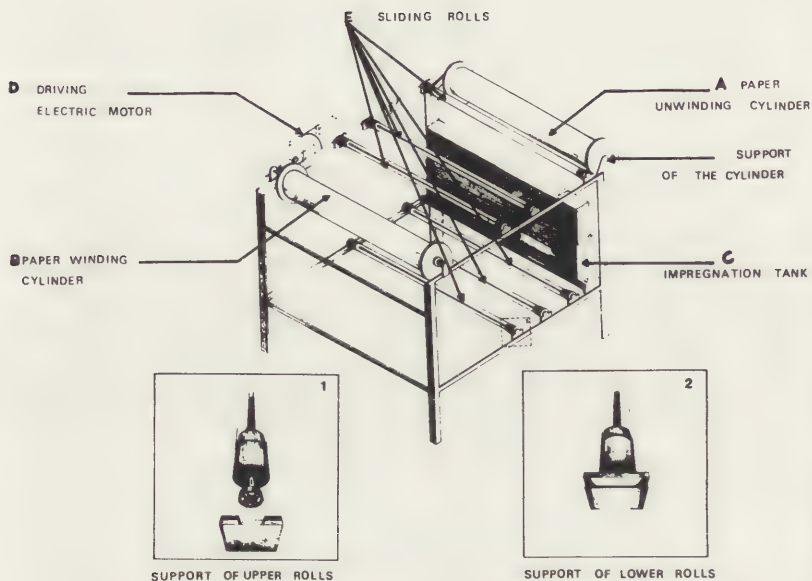


Fig. 1 - Apparatus for paper impregnation and details of volving bearings.

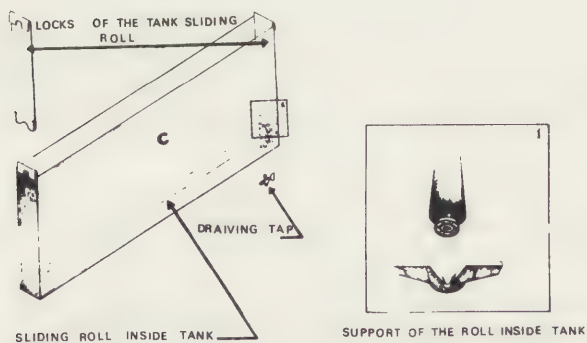


Fig. 2 - Impregnation tank and interior roll detail.

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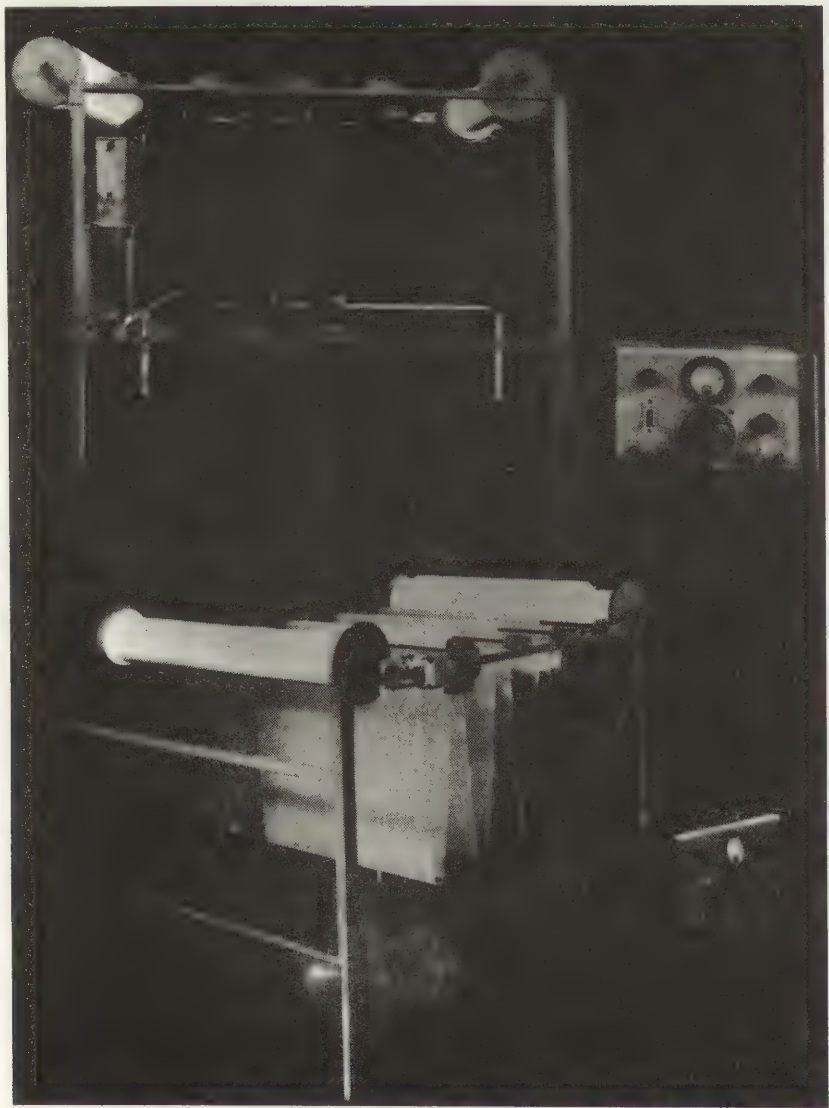


Photo 1-2 - Paper impregnation apparatus without and with the paper.

paratus is working. Once this is done, the end of the paper is passed over the first glass roller, which should be positioned so that the paper is drawn against the edge of the tank as it emerges. In this way the solution will be evenly distributed on the paper during the impregnation process. The end of the paper is then treated over and under the other rollers until it reaches cylinder B, to which it is fastened with a bit of glue. The lower rollers are slightly offset in respect to the upper ones.

After the paper is positioned, the solution is poured into the tank until it completely covers the metal roller. Two liters of solution are sufficient. At this point the motor can be started and the impregnation begun.

Preparation of the impregnating solution

The solution is prepared by dissolving 14.3 gr of Paraloid at room temperature in one liter of tetrachloroethylene. The dissolving is very slow, so that it is advisable to put the solvent and the solute in a closed container which is shaken from time to time; it takes two or three days for the Paraloid to completely dissolve in this fashion. Clearly, it is necessary to close the container with a plug that is not soluble in the solvent. The solution obtained in this way has a density, measured at 27°C, of 1.560 gr/cm³, as can be deduced from the graph given in fig.3.

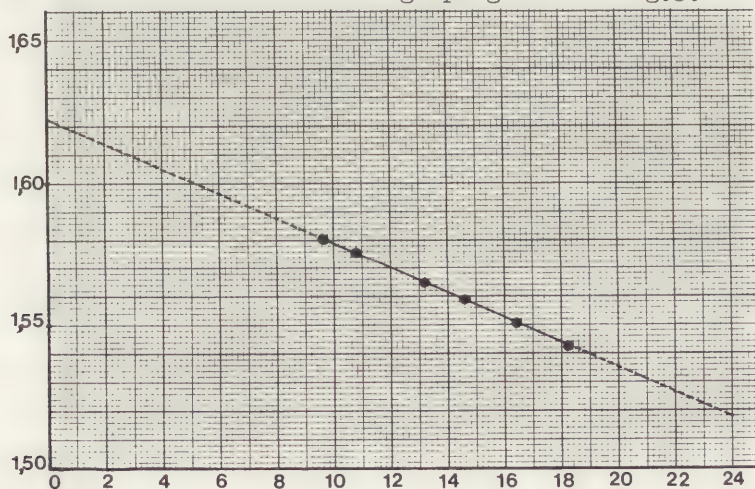


Fig. 3 - Impregnating solution density according its concentration.

Measurement of the density of the solution can be a useful way to measure its concentration as long as the measurements are always taken at the same temperature. In fact, the density of the solution varies notably with variations in temperature. As can be seen in fig.3, lower densities correspond to more concentrated solutions. This is due to the fact that the solvent, tetrachloroethylene, has a higher specific gravity than the solute. The concentration chosen, of 14.3 grams of solute added to 100 cc of solvent, is the most suitable concentration for our purposes; it is advisable not to stray too far from the indicated values so as to avoid the problems described below.[†] If the solution were more highly concentrated there would be two drawbacks. As the paper moves through the machine, it could stick to the drying rollers and then tear; moreover, even if one were to succeed in impregnating the paper with a higher concentration than that suggested, it would overload the paper with the solute and after dry bonding a document would appear translucent, as if it were bonded to a sheet of plastic. In the opposite case -- i.e. when the concentration of the solution is too low -- the treated paper would be likely to separate from the document after dry bonding. The exact concentration of the resin can also be ascertained under the microscope. In this case, as shown in photo 3, the resin covers the cellulose fibers of the paper but does not fill the largest spaces formed by casual interweaving of the fibers.

While the machine is working, it is important not to stop it for any reason, because the sheet of Japanese paper would then stick to the drying rollers. If, for some reason, the operation must be interrupted before all the paper has passed from cylinder A to cylinder B, it is better to cut the paper quickly with scissors before it enters the tank and keep the apparatus working until the tail of the treated paper has been rolled onto cylinder B.

[†] N.B. - the concentration is not given in gr/100 cc; that is, a given quantity of solute is not measured and placed in a graduated container, to which solvent is added up to 100 cc in volume. Instead, 100 cc of solvent is added to the solute so that the final solution's volume is 100 cc plus the volume of 14.3 gr of solute, which is about 10 cc, given the low specific gravity of Paraloid.

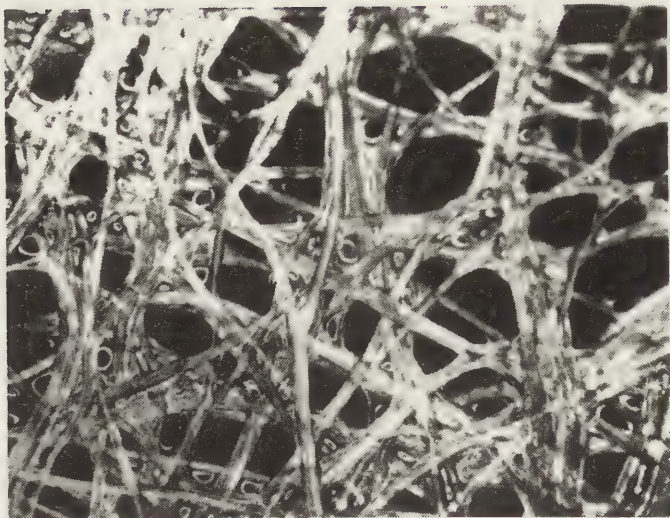


Photo 3 - Treated Japanese paper seen at microscope. It is evident that resin covers fibers without closing larger holes, as it happens when impregnating solution is too highly concentrated.



Photo 4 - The same quality of paper of photo 3 seen at microscope before impregnation.

PART II

RESTORATION OF FRAGILE DOCUMENTS WITH THE DRY BONDING METHOD

Dry bonding of thick paper.

Utilization of Japanese paper, prepared as described in Part I of this article, is fairly simple; it permits fragile documents to be restored in a rapid and reversible manner and, above all, without losing original fragments.

The sheet of paper being restored is placed between a sheet of treated Japanese paper and a sheet of silicon paper. Another sheet of silicon paper is put over the Japanese paper. Two pieces of thin cardboard complete the outside of the sandwich. The whole is placed between the heated plates of a hydraulic press that can exert a pressure of about 25 Kg/cm^2 for one or two minutes; the length of time the sandwich remains in the press can be increased or decreased depending on the thickness of the protective cardboard. After pressing, the silicon paper is carefully taken off by hand. It is easily removed from the Japanese paper, for Paraloid does not adhere to silicon paper; sometimes it is more difficult to remove from the restored document side, especially if the document is extremely decayed. In such cases it is better to replace the second sheet of silicon paper with cellophane, which does not adhere to the document under these conditions, although it makes the restored sheet slightly translucent. Mainly because it is unnecessary, but also for this reason, it is better not to put the cellophane next to the treated Japanese paper.

Sometimes it is necessary to bond both sides of a document when it is extremely weak or the old paper is very thick. However, we have found that bonding one side alone suffices in most cases. Once bonded, the document can be immersed in water for ulterior operations of washing and deacidification that would have been impossible before. We have found that documents can be washed and deacidified even when they are bonded on both sides, for the bonding is permeable to aqueous solutions; one need only prolong the immersion time somewhat. The only drawback arising from water baths is that the transparency of the Japanese paper is diminished and thus the legibility of the document is attenuated. However, transparency is again improved if, after drying, the bonded document is returned to the heated press. On the other hand, we have found that the Japanese paper can be instantly detached, even after twelve days of artificial aging at 105°C , through simple immersion in

acetone or in another Paraloid solvent whenever acetone cannot be used for fear of discoloring inks or pigments.

After bonding and eventual deacidification, if missing parts of the document must be repaired, it is advisable to cut away the Japanese paper with a restorer's knife in the area corresponding to the missing part. After this, it is possible to fill in the missing areas using normal manual restoration techniques. The impregnated Japanese paper should be removed first because the water-base adhesives normally used for repairs do not adhere tenaciously to Paraloid.

This technique was used to restore a volume, conserved in the Bologna University Library: "Le Neptune Francois, ou Atlas Nouveau des Cartes Marines pour l'Usage des Ermees de Mer - 1693". The water-colored maps were particularly fragile and browned, especially where some copper base pigments were used. The colors were generally soluble in every solvent. The average pH was around 4,5 - 5. Except in a few cases, the maps were bonded only on the back; then they were deacidified by suspending them on the surface of a solution of calcium hydroxide just long enough for the liquid to penetrate the paper without dissolving the colors. After drying, the missing parts were reintegrated as described above.

Dry bonding of documents.

If the paper to be bonded is under 0.1 mm thick, reintegration of missing parts can be done automatically in the hydraulic press, using Japanese paper of a quality and thickness suited to the characteristics of each document. In such cases, while preparing the sandwich for the press, one can position the repair paper facing the impregnated Japanese paper. It should be large enough to fill the entire missing area and overlap it by a few centimeters. While in the hot press this repair paper will also adhere to the impregnated paper and fill in the hole. At this point the restorer need only trim away the excess paper with a suitable knife and finish the edges of the hole by brushing glue around them.

Acknowledgement

We wish to thank miss S. Villanti and Mr. P. Barbato for the drawing's execution; Mr. G. Donati for the pictures.

We are particularly grateful to Mr. F. Nappa and to Mr. F. Losappio who built the apparatus and collaborated to the solution of many constructive problems.

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LE JOINTOIEMENT DES LEZARDES DANS LES
PEINTURES MURALES PAR LE JOINT-MASTIC
A LA BASE DU POLYURETHANE

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Zagreb, 1978



LE JOINTOIEMENT DES LEZARDES DANS LES PEINTURES MURALES PAR LE JOINT-MASTIC A LA BASE DU POLYURETHANE

Ivan Bogovčić

Pendant les tremblements de terre en 1976 qui ont atteint le nord-est de l'Italie et le nord-ouest de la Yougoslavie, un grand nombre d'objets culturels et historiques a été endommagé. Parmi ceux il y a aussi des peintures murales, qui ont été atteintes et dont la plupart s'est crevasée fortement.

L'assainissement statique des murs est fréquemment achevé par une injection d'une masse cimentaire dans les murs ébranlés et par le reliage, ou bien par l'ancrage de ceux-ci.

Comment protéger les peintures murales du danger d'écoulement de la masse cimentaire à travers les lézardes sur les peintures murales? Le traité suivant essaie d'expliquer la méthode de jointoiment des lézardes par le joint-mastic à la base du polyuréthane.

□ □ □ □ □

Pour la consolidation statique des murs on a commencé, après le tremblement de la terre, à introduire un système spécial du reliage, de l'ancrage et des injections d'une masse cimentaire. Ce système a été développé par L'Institut pour les recherches des matériaux et des constructions de Ljubljana (RS Slovénie). Pendant l'assainissement après-sismique la firme "Benedil" de Cividale del Friule (Italie) a commencé à l'appliquer.

Parmi autres, cette firme a assaini un bâtiment, qui a été endommagé pendant les tremblements de terre et qui a été orné des peintures murales du 18^{ème} siècle. Le crépi peint s'était crevasé déjà avant les tremblements, mais les

lézardes ont été stuquées et retouchées. Pendant les tremblements en 1976 de nouveaux dégâts - de nouvelles lézardes ont apparu aussi.

L'injection des murs se fait dans la règle des deux côtés du murs. Chez les murs peints l'injection se fait exceptionnellement seulement de la part non-peinte. Malgré ça, la masse cimentaire a menacé de pénétrer à travers les lézardes côté peint et d'endommager les peintures murales.

Aux conditions normales les lézardes pourraient être stuquées de la façon classique avec de fin mortier calcaire-sabloneux et, selon le besoin, injectées du côté de la peinture avec une solution de caséinate.

En employant le système mentionné de reliage et d'ancrage des murs il en vient aux déplacements, même au cours de reliage ainsi qu'au cours d'ancrage. C'est pour ça que le stuc classique, qui est dur et fragile, pourrait facilement se détendre sous ces tensions et ne pourrait plus empêcher la masse cimentaire de pénétrer à travers les lézardes sur la surface.

En cherchant une solution convenable, je me suis décidé pour la méthode suivante, laquelle j'ai proposée à la commission, qui l'avait acceptée. J'ai fait emploi d'une matière qui s'utilise avec du succès sur beaucoup de sphères d'activité. J'ai fait emploi de joint-mastic à la base du polyuréthane ("Sikaflex la"). Je me suis décidé pour cette matière surtout à cause de ses qualités primaires - l'élasticité et une bonne adhésion. J'ai fait emploi d'une telle sorte du stuc, qui en durcissant ne sécrète pas des résidus d'acidité.

Le procédé du jointolement des lézardes s'est passé comme suit. Si c'était nécessaire, on a approfondi et élargi les lézardes. Après le dépoussiérage on a appliqué du "primer" sur les côtés des lézardes, 3-4 mm sous le niveau de

la peinture. Après le séchage du "primer" on a placé dans les lézardes une cordelette, qui a fermé les lézardes à peu près dans la profondeur d'un centimètre sous le niveau. Après on a joint les lézardes avec le joint-mastic à la base du polyuréthane. A la distance de 30 cm approximativement ont été placées dans toutes les lézardes (à travers le stuc) de courtes ficelles plastiques (7-8 cm). Après le séchage on a fait à travers ces ficelles l'injection avec la solution de caséinate pour renforcer ainsi la barrière, laquelle devrait empêcher la masse cimentaire de pénétrer la surface peinte (fig. A).

L'avantage de cette méthode est surtout l'élasticité du tampon dans la lézarde, lequel, à cause de sa neutralité, reste pour toujours installé sous les peintures murales.

Une fois la consolidation statique accomplie, on met dans les lézardes sur la couche du joint-mastic à la base du polyuréthane encore le classique stuc calcaire-sablonneux final. C'est à cause de cela, que le joint-mastic à la base du polyuréthane doit être placé assez profondément, pour que le stuc classique puisse avoir assez de crépi libre pres de côtés des lézardes pour se joindre avec lui.

Même la surface du joint-mastic à la base du polyuréthane peut être bien préparée pour un meilleur enchaînement avec le stuc classique. On peut l'obtenir en appliquant le joint-mastic à la base du polyuréthane avec une solution de résine, sur laquelle on applique du sable fin ou bien des flocons de coton. Il est mieux d'appliquer le sable, parce que le coton absorbe et dégage trop d'humidité et à cause de cela il en vient aux permanents micro-déplacements dans le volume du stuc classique. Le stuquer accompli, il faut encore retoucher les lézardes.

Au moment il est impossible de donner une appréciation finale sur tous les côtés positifs et négatifs de cette

méthode. Le procédé seul d'application du "primer" et de placement du joint-mastic à la base du polyuréthane demande une précision extrême. Surtout il est important, que la "primer" soit appliqué solidement, sans aucun espace libre, car le joint-mastic à la base du polyuréthane ne se lie pas aux surfaces non-adhésives. La masse d'injection peut pénétrer la surface à travers ces endroits défectifs et endommager la peinture.

Le désavantage de cette méthode consiste en ce que les côtés des lézardes doivent être solides et ne doivent pas se décrépir.

En somme, les qualités positives de cette méthode, respectivement de cette matière sont toutefois telles, qu'il serait opportun d'employer cette méthode non seulement en cas d'assainissements sismiques, mais aussi en cas d'autres assainissements des peintures murales, où une injection doit être fait.

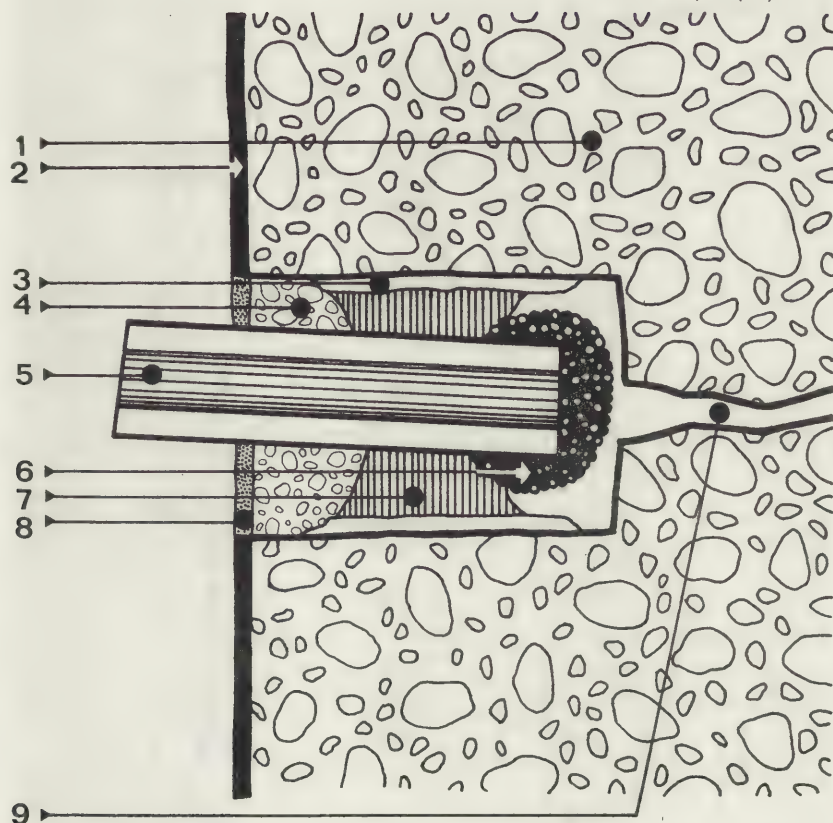


figure A : coupe transversale (cca 1:6)

1. crépi original
2. couche original de la couleur
3. »primer«
4. stuc classique (chaux, sable)
5. ficelette
6. cordelette
7. joint-mastic à la base du polyuréthane
8. retouche
9. lézarde

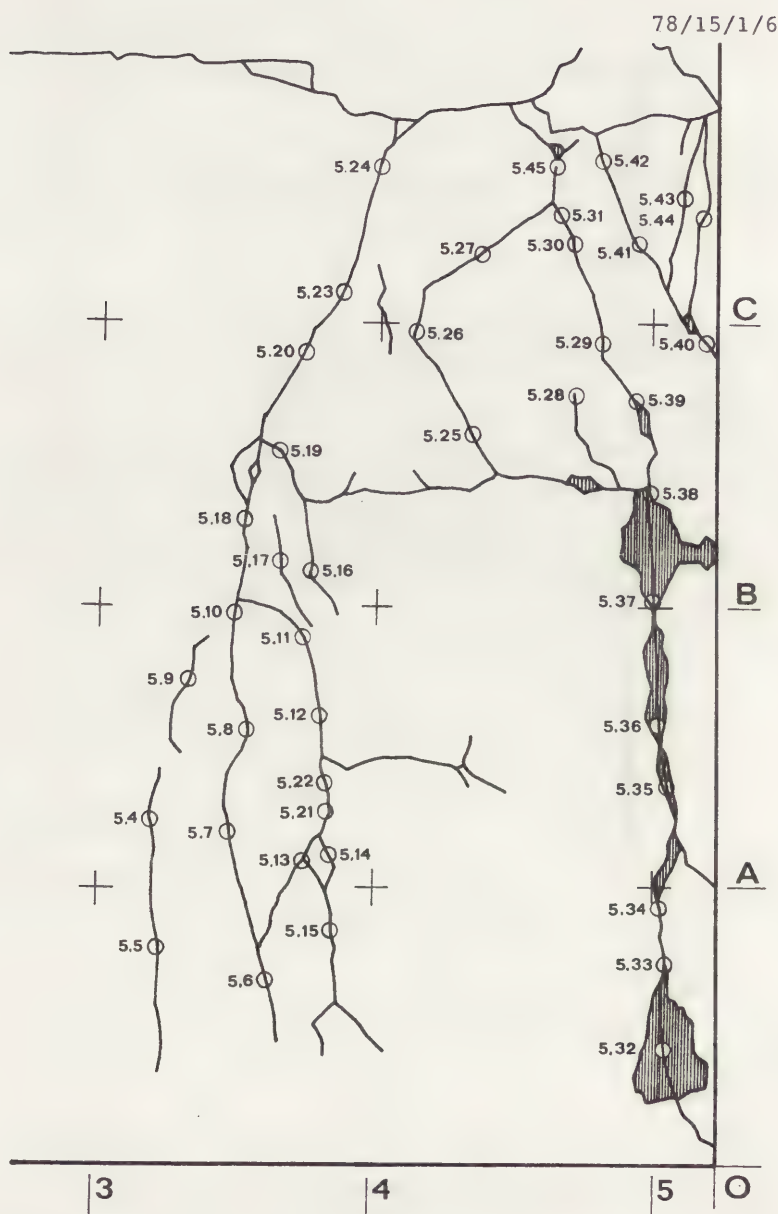


figure B

Détail du mur avec des lézardes traitées et des ficelles numérotées
(PALAZZO COMUNALE DI CIVIDALE DEL FRIULI)

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'MONUMENTALES PASTELL' - A FORGOTTEN
INVENTION IN WALL-PAINTING-TECHNIQUES
ABOUT 1900

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Zagreb, 1978

'MONUMENTALES PASTELL' - A FORGOTTEN INVENTION IN WALL-PAINTING-TECHNIQUES ABOUT 1900

M. Koller

Abstract

1905 in Munich a booklet was edited by Wilhelm Ostwald about "Das monumentale Pastell", a newly invented uncomplicated wall-painting-technique. He describes the drawing on dry plaster with selfmade thick colour-sticks bound with casein and their fixing with casein-solutions. The Beethovenfrieze by Gustav Klimt, 30 meters long and executed in 1902 with delicate subtleness for a great exhibition in the "Secession" in Vienna, seems to be the unique important piece of art representing this interesting wall-decoration-technique about 1900 in the time of Art Nouveau-style. Refers to similar examples and related problems are welcomed for the restoration-works now in progress.

The actual restoration of the so called Beethovenfrieze a painted homage of its 9th symphony by Gustav Klimt now in the workshops and laboratories of the Bundesdenkmalamt in Vienna, puts at first the question of its painting-technique. This impressive work of about 2,2 to 30 meters size was originally executed only for the 14th exhibition of the artists union "Secession" in Vienna. It remains remarkable although no details have been kept that at first a presentation of contemporaneous frescoes was planned but

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not realised instead of the Beethoven-celebration (1). The center of this at 15th April 1902 opened XIV exhibition formed the famous Beethoven-Sculpture by Max Klinger, now in the Leipzig Museum. The diaphane Room-annexes showed paintings of the secessionists, in the first of which below the elevated frieze of Klimt, that closed the top of the walls where other paintings and compositions of carved cement, mosaik, intarsia, sgraffitto, surrounded and contrasted all with a very rough structure of pure white-washed wall-plaster. Musical performances in the exhibition rooms, directed by Gustav Mahler, raised this temporary performance to the totality of the arts (in the sense of Richard Wagner) in favour of the genius composer (2). After this exhibition a few months later the frieze has been cut into 8 pieces from 3 to 7 meters to transport them away. Since that event up to 1974, when our examinations started, it has been kept in several depots and suffered various damages. After restoration, this painted monument of Austrian music and its artistic estimation in the early 20th century will be definitely exposed in a separate part of the recreation centre of the newly built UNO-City in Vienna.

Returning to technical problems we have to recall something about the revival of baroque techniques of monumental murals at the age of "Historismus", especially in the important buildings of the "Ringstraße" in Vienna (3). Great cartoons, "spolvero" and square nets were used for executing the designed compositions, but only a few artists like Schwind or Rahl used real fresco technique too. (4) Oil-painting onto "marmorino-" or gesso grounds and "marouflage" (oil-paintings on canvas stuck to the walls or vaults by means of oily pastes like lead-white) are surplus in number. As the young Gustav Klimt did in his early works on the staircases of the Burgtheater (1887) and the Kunsthistorische Museum (1891) in Vienna, before he took part at the institution of the "Secssion"-group in 1898 (5).

The support of the Beethovenfrieze consists, like baroque illusionistic wall-paintings, of a simple construction of

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of unplanned wooden planks with stucco-reed-mats nailed on. The latter bearing the lime-plaster (with a small content of gypsum), which became very smooth with a steel-board as usual in plaster-crafts. As no "giorante" or "pontate" can be observed and according to the dimensions and some details of execution this plaster must have been totally dry at the beginning of the painters work. This was started with a charcoal-underdrawing of local areas in one tone but shows in majority only different coloured lines, delicate in their rythm and tonality, which are characteristic for the Viennese style of Art Nouveau ("Jugendstil"). These lines are difficult to define in their origin from a pencils or/and a sticks mark and have been put on in several layers to form an impression of non-mixed pale colours. Sometimes on top of that final graphite-lines additional drawings can be seen. Rich guilding with and without transparent colour-layers above, gypsum-ornaments and applicated glass- or precious-stones were used for final enrichments. Regarding the materials on work the catalogue of 1902 only speaks about casein-colours on plaster with stucco and precious-stone applications. Unnecessary to confirm for a painting of conscious modern mind like this that there is no surface-coating or colour-brightness at all. The soft matness of the colours unifies with the great areas of unpainted gray plaster and contrasts to the shiny gloss of the precious stones. This drawn painting is quite different from and much more subtle than traditional secco-techniques. It remembers evidently to the graphic arts like crayon-drawings, lithographs and most of all to pastel-paintings (6).

This unusual but modern aspect stimulated to look for similar evidence. Following one of the numerous traces collected in the vaste compilation book of Eibner (7) I came across the invention of "Das monumentale Pastell" in contemporean Germany by the colour-physicist and important painting - theorist Wilhelm Ostwald. Ostwald published his experiences

first in 1905 in a newspaper and after some painter had worked in that manner with very good results he edited a booklet in Leipzig 1912, to which I am able to refer (8). The plaster should contain an addition of pumice-stone-powder and finally be smoothed with felt and thinned lime-milk. After full carbonisation the drawing with the coloursticks could start. The coloursticks had to be made with normal fresco-pigments, using only chalks for white and dextrin, tragacanth and gummi arabicum as binding-mediums. The painter can easily do this for himself selecting the scale of colours and tones after his purpose. When the painting is finished he has to blow off the loose parts and then start with the process of fixing. This has to be done with an aqueous borax-casein-solution containing a quarter of alcohol and afterwards hardened by aluminiumacetate or formaldehyd. All these operations should be performed several times avoiding any oversaturation, drops or coarseness. For outdoor-murals at least an impregnation with paraffin-wax should be used.

In this way before 1911 several attempts have been made in Jena, Berlin, Hamburg, Mannheim und Schaffhausen (outdoor-paintings), their stage of conservation nowadays would be of interest to know.

The creation of Klimt's Beethovenfrieze took place in Vienna only 3 years before the first model of Ostwald's invention and its technique is quite close to the later description. The interesting problem of priority is worthwhile further discussions. The relation of the secessionists in Vienna to their art-friends in Munich, Leipzig or Berlin and a great number of other European countries too are known to have been frequented both by visits and exhibitions, but no other mural following the "monumental pastel"-technique is known in Austria. Klimt's work from 1902 seems to be the one of the rare examples of this kind preserved as far as we know at the moment. Klimt designed a second frieze in

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1910 for the dining room in the famous Palais Stoclet in Brussels, built by the Viennese architect and designer Josef Hoffmann. There he did not use this technique once more but drew only the natural size cartoon with detailed descriptions for its execution in mosaic, which is now kept in the Kunstgewerbe Museum in Vienna. (9).

The restoration of the Beethovenfrieze is now in the second step of its realisation. A first piece of the 8 compartments is ready and demonstrated the difficulties of dimensions and non-altering fixation of the mat surface aspect. Further examinations and experiments have now started again and Dr. Ivo Hammer as restorer and Dr. Hubert Paschinger as chemist are together with the author in charge of the further restoration of this complex work. We all will be indebted in gratitude to all colleagues giving any useful note or address of similar wall-paintings of that time with related problems.

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Gustav Klimt, Beethovenfries 1902: Detail of a gliding genius before restoration 1977



LES MATERIAUX DE PEINTURE DE LA CAVERNE D'ALTAMIRA

José María Cabrera Garrido

ABSTRAIT

Les observations qui se sont accumulées sur les couleurs des peintures ainsi que l'analyse des pigments trouvés dans les fouilles archéologiques de la caverne jusqu'en 1925, ont permis d'affronter l'identification des constituants des polychromes. On étudie une gamme de couleurs qui comprend le Noir, Blanc, Gris, Violet, Rouge, Rose, Marron, Jaune, ainsi qu'un colorant organique violet et l'utilisation comme possible pigment de l'ambre moulu.

OPINIONS SUR LA TECHNIQUE DES PEINTURES.

Pour M. Marcelino Sanz de Sautuola (1880) (1), elles sont peintes "apparemment avec de l'ocre noire et rouge". Le Professeur Harlé (1881) (2) opine qu'elles sont tracées avec de l'ocre rouge et du charbon, utilisant un pinceau. M. Vilanova (1882) (3) dit qu'elles furent faites avec des ocres naturelles noire, jaune et rouge, et M. Lemus (1886) (4) croit qu'elles sont faites au pinceau et avec du noir de fumée ou d'os ; ces opinions étant parmi les plus représentatives des premiers études basées sur l'observation des peintures avec l'éclairage des bougies.

Plus tard, utilisant des lampes à l'acétylène, Cartailhac et Breuil (1906) (5) distinguent des ocres de couleur rouge, noir, marron et jaune varié, appliquées au pinceau.

Avec l'aide de la lumière électrique, et utilisant des projecteurs mobiles, Breuil et Obermaier (1925) (6) réalisèrent une étude minutieuse, observant certains tons violacés des ocres et quelques taches encore plus violettes. Pour eux, les artistes employèrent comme matières colorantes le charbon végétal, si abondant dans les foyers; l'ocre et l'hématite leur fournirent le rouge, le jaune et le brun; il n'y a ni bleu ni vert mais bien quelques tons violacés possiblement tirés du manganèse. Concernant la technique d'application utilisée, ils pensent que ces matières furent, ordinairement, réduites en fine poudre à laquelle on ajouta des substances collantes (graisse, résine, sérum de sang, jus végétaux, etc..) pour obtenir, par le feu,

une pâte semi-liquide susceptible d'être appliquée à la roche avec le doigt ou avec un vrai pinceau, exécutant ainsi une sorte de peinture à l'huile.

Pour Pietsch (1964) (7), il est très difficile de définir exactement les nuances chromatiques observées car elles dépendent non seulement des différentes "températures de couleur" des divers éclairants mais aussi des variations dans le "contenu d'humidité" dans les peintures. Pour lui, l'ample gamme de couleurs depuis le jaune jusqu'au violet passant par le marron et le rouge sont de l'ocre rouge ou ocre d'oxyde de fer et les colorants noirs, de l'oxyde manganique et charbon végétal. L'opinion du chercheur Martin est, d'après M. Pietsch, que ces oxydes de fer ou manganèse ont réagi avec la roche calcaire, se transformant en ferrite ou ferrate calcique et manganite ou manganate calcique respectivement, pouvant se classer comme un type de fresque naturelle.

En 1977, le Dr. Martí (8) analyse avec des techniques de Rayons X des échantillons pris du plafond dans la zone à droite de la grande crevasse et, de ce fait, hors du grand ensemble principal des polychromes, identifiant dans les échantillons de pigments et support les constituants suivants : 1) échantillon représentatif de support rocheux, un mélange d'Orthoclase et Carbonates de Calcium, Fer et Potassium; 2) peinture rouge avec Limonite et des traces de Goethite; et 3) peinture noire avec Mn_2O_3 et MnO ainsi que deux lignes qui purent appartenir à C, probablement des restes de charbon végétal.

D'un point de vue général, Margival (1959) (9) étudie les connaissances sur les pigments et les peintures de l'antiquité préhistorique, indiquant que, de toutes les couleurs utilisées, on peut seulement signaler les produits suivants :

Noirs: de charbon, d'os, de manganèse ; graphite.

Jaunes: d'ocre, d'oxydes de fer.

Marrons: argile ferrugineuse.

Blancs: Calcaires, Plâtreux, Kaolinitiques.

Rouges: ocres, oxydes de fer.

LES PIGMENTS DES FOUILLES D'ALTAMIRA.

Au début du siècle, M. Hermilio Alcalde del Río (10) réalise des fouilles à Altamira et obtient entre beaucoup d'autres choses importantes des résidus de charbon d'os et de très abondants fragments d'ocre de fer "qui ont supposé plus de trois kilos", dont certains, avec de marques d'avoir été utilisés. Il obtint aussi de nombreux cailloux tachés d'ocre qui servirent pour préparer la couleur, tandis que le manganèse et le jaune

d'ocre ferreux ne furent trouvés qu'en minime quantité.

Dans les fouilles de 1924-1925, le Professeur Obermaier - (11) trouva "des crayons d'ocre rouge et jaune de diverses nuances, charbon de bois et marne blanc grisâtre (qui) représentent la matière utilisée pour la confection des couleurs". Dans un rapport de 1929 (12) M. Obermaier nous dit qu'on a trouvé aussi - "des restes d'ambre, des fossiles et du cristal de roche ainsi - que des matières colorantes, ocre, oxyde de fer et marne. Une - partie de ces matières colorantes se présentent brutes et sont ensuite travaillées en les triturant et en les mélangeant à des graisses ou du sang; d'autres sont de vrais "crayons à dessiner" car elles sont aiguisées à leurs extrémités".

Cette collection se conserve actuellement dans deux boîtes du Musée d'Altamira. Pietsch (7) publie une bonne photo en couleur de quelques échantillons parmi lesquels on voit le rouge, noir, gris plomb, blanc ivoire, sous le titre "échantillons d'ocre et manganèse de la grotte d'Altamira".

Une description plus nuancée de ces échantillons, les classant en groupes aussi homogènes que possible, nous servira de référence pour tout ce qui concerne leur étude:

1.- Vingt-deux fragments d'ocres terreuses de divers tons (dans une boîte tous ensemble, ils semblent moins importants que le reste des échantillons qui sont dans l'autre boîte).

2.- Six marceaux de pierre d'Hématites, très durs et avec des traces d'avoir été grattés intensément sur diverses faces.

3.- Trois fragments d'Oligiste de couleur rouge violacé, tous très durs et avec des traces d'avoir été grattés sur une face.

4.- Quatre fragments d'ocres, assez compacts et avec de possibles râclures, de tons rouge intense, marron, jaune foncé et jaune clair, respectivement.

5.- Trois coquilles de patelle contenant des restes de pigments préparés, deux avec des taches d'ocre rougeâtre et une avec un peu de couleur noire.

6.- Une coquille de patelle pleine de pigment préparé, de couleur blanche, montrant à la surface des marques comme de griffes, causées par des filaments grossiers. Une pâte de pigment blanc préparé, similaire à l'antérieure et avec l'aspect d'avoir été détachée de sa coquille de patelle.

7.- Pâte de pigment de couleur gris plomb, pétrie en forme de petit pain, avec la surface très lisse et où l'on peut voir des griffes comme celles du blanc.

8.- Deux petits fragments de pigments préparé de couleur rose.

9.- Une dent de cheval carbonisée.

10.- Un marceau d'ambre en forme de masse arrondie, très - crevassée et fragile.

Résultats analytiques:

Les méthodes employées sont, schématiquement : Diffraction de Rayons X, en diagrammes de poudre et techniques d'Agrégats Orientés, avec Ethylenglycol et traitement thermique pour les minerais d'argiles, analyse élémentaire semi-quantitative par spectrographie d'émission ($\lambda\beta$) et microscopie optique. Les résultats obtenus nous indiquent ce qui suit:

Groupe 1.- Ces vingt-deux fragments d'ocres, terreuses et peu compactes, contiennent de l'eau en quantités variables supérieures à 6%. Comme éléments minéraux, ils contiennent de l'Hématites et de la Goethite et sont rendus impurs par des minerais d'argile, Quartz et Oxydes de Manganèse principalement, contenant aussi, des quantités variables de Carbonates de Calcium et Magnésium. Bien que la proportion de tous ces constituants varie considérablement des uns aux autres, selon notre point de vue, il semble que la couleur rouge soit due à l'Hématites et, au fur et à mesure que sa concentration diminue et qu'augmente celle des autres minerais, l'intensité du rouge décroît jusqu'à des teintes marron ou jaunâtre. Dans les plus jaunes, la couleur est due fondamentalement à la Goethite, les Carbonates augmentant considérablement.

Groupe 2.- Tous ces "crayons" ont donné aux Rayons X une composition similaire, avec plus de 95 % d'Hématites et une petite quantité de Micas comme minerais des argiles. Ils sont d'une matière très compacte, d'aspect externe marron mais de couleur rouge intense à la partie grattée, avec des particules très fines, opaques à la lumière transmise, avec des traces de Mn, Ti et Cu et un contenu en eau pratiquement nul.

Groupe 3.- De couleur rouge violacé, très compacts et presque sans humidité, ils ont une composition minéralogique d'Hématites (plus de 90 %) et Quartz. Au microscope, nous voyons de grands cristaux transparents, d'un rouge très vif et leur composition élémentaire montre, outre le Fer et le Silicium, $Al = 1,7\%$ $Mn = 0,35\%$, $Mg = 0,2\%$, $Ca = 0,15\%$ et des traces de Cu, en moyenne.

Groupe 4.- Des ocres relativement compacts mais faciles à désagréger dans le mortier, ont la composition suivante: le "rouge intense" est à base d'Hématites, Calcite et Dolomite, étant en

réalité un mélange de Carbonates rendus impurs par de l'Hématite donnant une couleur rouge très vif; le "marron" contient du Quartz et des Hématites à peu près dans la même proportion, quelques Hydroxydes de Fer comme la Goethite et amorphes et un peu de Micas comme minerais accessoires; l'échantillon de couleur "jaune foncé" est formé fondamentalement par de la Goethite, et l'on voit au microscope une petite proportion d'amorphes et minerais d'argile, et le "jaune clair" contient de la Calcite, Dolomite et une très faible quantité d'Hydroxydes de Fer, qui sont seulement vus au microscope comme amorphes, l'échantillon présentant, en général, l'aspect caractéristique de quelques altérations de Carbonates où le Fer se présente comme impurifié.

Groupe 5 .- Dans les taches rouges on identifie de l'Hématite. La pâte de couleur Noire adhérente à la coquille de patelle, examinée dans le binoculaire, montre une composition terreuse, imprégnée de particules de charbon de divers formats et mêlée à des petits morceaux d'os, fragments de coquilles, etc. Dans son aspect et composition générale, elle est très semblable à la terre noircie de la zone de fouilles dans la caverne, composée aussi par des résidus d'aliments et charbons du foyer. Parmi les restes charbonneux il y a quelques particules de format suffisant pour montrer que la structure est ligneuse; d'autres, très rares cependant dans cet échantillon, montrent une structure compacte et laisse un abondant résidu à la calcination où l'on identifie des Phosphates, ce qui permet de les identifier comme provenant de la carbonisation d'os, dents, cornes ou autres éléments d'origine animale.

Groupe 6 .- La couleur blanche est une pâte composée fondamentalement par des Micas (78 %) et du Quartz à grain très fin (22%) montrant une structure filamenteuse très différenciée. L'étude de Rayons X avec techniques d'A.O. montre que les phyllosilicates de l'argile sont fondamentalement une Illite de bas degré de cristallinité. L'examen microscopique montre, mêlés au pigment, de petits et pas très abondants fragments de matière organique, anguleux, transparents et de couleur jaune claire, semblables à l'ambre moulu que nous verrons plus loin. Le pigment se défait facilement dans l'eau froide mais, dans la solution ni froide ni chaude nous ne trouvons aucun type de composé organique auquel nous pourrions attribuer une fonction de liant. L'autre échantillon de pigment blanc a les mêmes caractéristiques.

Groupe 7 .- La pâte gris plomb a une composition minérale semblable à celle des échantillons de couleur blanche, mais présente quelques différences; les Micas représentent 75 % environ (dont le 90 % est une Illite avec un degré de cristallinité plus

haut que dans les échantillons antérieurs de blanc, et un 10% est de Montmorillonite) et plus de 20 % est de Quartz ; on voit aussi au microscope la présence de particules d'Ocre et de charbon auxquelles on devrait peut-être attribuer l'obscurcissement ajouté. Comme précédemment, on observe au microscope de petits et très rares fragments d'une matière similaire à l'ambre moulu. L'échantillon se défait facilement dans l'eau froide, mais on ne peut extraire un produit organique assimilable comme étant un possible liant.

Groupe 8 .- Ce pigment rose a une composition minéralogique à base de Calcite, Kaolinite, Quartz et Chlorite. Le microscope montre un peu d'ocre rouge et un peu de Charbon , capables de justifier le ton de l'échantillon. Il se défait à l'eau froide qui ne laisse pas de résidu utile en s'évaporant. Au microscope nous voyons aussi des particules similaires à celles de l'ambre, comme dans les autres échantillons.

Groupe 9 .- Un morceau de charbon animal, identifiable par son aspect externe avec les dents de cheval qui apparurent lors des fouilles. En triturant ce charbon, on obtient un pigment noir similaire, en toutes ses caractéristiques extérieures, microscopiques et microchimiques, à celui que nous identifions comme noir animal dans divers échantillons d'Altamira.

Groupe 10.- Ce morceau d'ambre est sans doute celui qui fut recueilli par Obermaier en 1925. Il a pu être identifié par le Dr. John S. Mills (14) avec un échantillon d'ambre étudié par lui, il y a des années, et qui est conservé au British Museum (Natural History) n° 21339 "Spanish Ambar from near Santander" et fut ensuite comparé avec succès à des échantillons du Musée de Sciences Naturelles de Madrid, provenant de la côte de Comillas et du carbonifère de Santander. Pour le Dr. Mills, c'est une authentique résine fossile provenant de l'un ou l'autre type de conifère, et les différences que l'on remarque dans le spectre d'absorption I.R., spécialement l'ample bande d'absorption que présente celle d'Altamira entre 1530 et 1680 cm^{-1} démontre qu'il faut l'attribuer à des groupes carboxyles ionisés qui, en raison de son comportement comme une résine naturelle à changement ionique, ont réagi dans le sol calcaire et humide d'Altamira formant le sel calcique du polymère.

LES PIGMENTS DU PLAFOND DES POLYCHROMES

Nous basant sur les précisions établies, nous avons examiné le plafond d'Altamira très attentivement, d'abord à l'œil -

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nu, ensuite dans quelques parcelles, à l'aide d'une loupe bino--
culaire, constatant que presque toutes les couleurs trouvées -
dans les fouilles y sont représentées. On pourrait faire quel--
que réserve sur l'existence de la couleur rose, car nous croyons
ne voir que quelques petites taches et, par sa composition à ba--
se d'ocre rouge comme élément colorant, elle a une composition -
qui est presque la normal pour n'importe quel point du plafond.

Pour abonder avec une technique plus pénétrante dans le -
sens de ces appréciations visuales, nous avons cru possible de -
renforcer l'analyse par l'observation au microscope d'impercepti--
bles échantillons pris aussi avec l'aide d'un microscope binocu--
laire.

Nous avons rejeté l'utilisation de techniques de Fluores--
cence de Rayons X directement appliquée au plafond de la caverne
avec un équipement portatif qui utilise une source radioactive.
Nous croyons que donner une dose de radiation à ces matières, sur
lesquelles il conviendra peut-être un jour d'appliquer de la Ther--
moluminescence pour dater les formations calcitiques ou quelques
autres qui ne sont pas encore prévues, doit s'éviter dans la me--
sure du possible et surtout quand il n'est pas raisonnable d'at--
tendre de cette technique une information de qualité supérieure
à celle du microscope optique, dans notre cas.

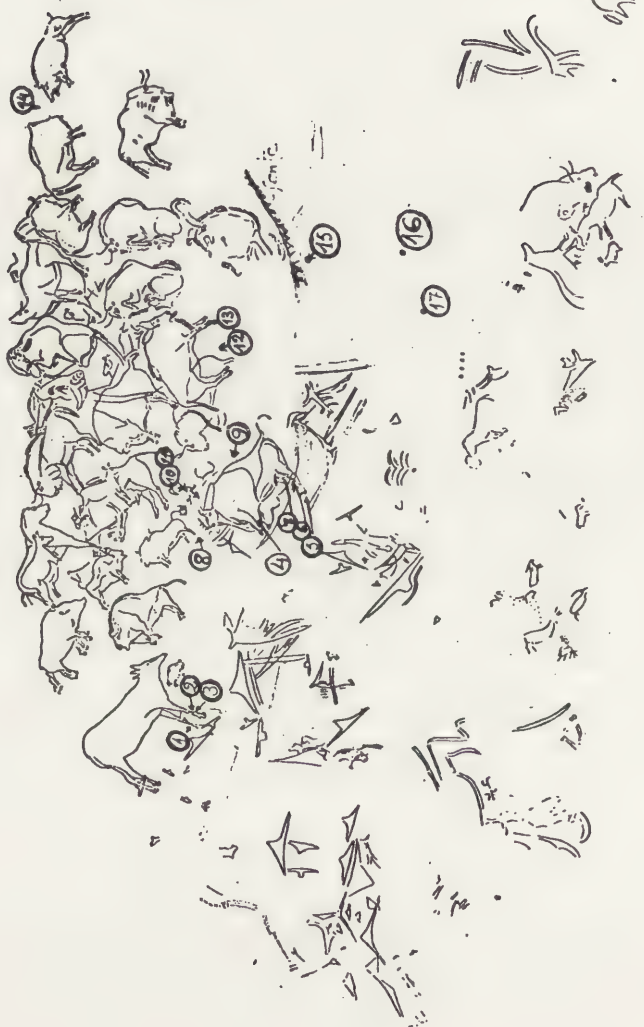
Pour cela, nous avons accepté la responsabilité de prendre
de très petites particules de couleur aux 17 points que nous in--
diquons sur le schéma en annexe, montant avec elles des prépara--
tion en Baume de Canada.

A la couleur Noire correspondent dix de ces échantillons, -
les numéros 1,2,3,4,6,7,8, 11,13 et 14. Dans tous les cas, les -
particules de pigment sont de Charbon, et il est impossible de -
différencier microscopiquement si c'est du charbon de bois ou -
d'os animaux car elles sont finement moulues. Dans l'échantillon
n°2 nous voyons aussi quelques très fines particules arrondies et
amorphes qui pourraient être de "noir de Fumée" : si nous pensons
aux bougies des visiteurs, on justifierait l'aspect abîmé de la -
peinture en ce point par une opération de nettoyage réalisée; pour
essayer de différencier si le Noir est de bois ou animal, nous -
avons appliqué à une petite particule du n° 1, un essai de Phos--
phates sur le résidu abondant de la calcination sur lame de Pt,
les résultats étant positifs, de sorte que nous croyons plus pro--
bable son origine animale dans les peintures du plafond.

Le rouge de l'échantillon n°5 est dû à l'Hématites, en par--
ticules très semblables à celles des râclures des "crayons".

Le rouge violacé de l'échantillon n° 10, se sont des cris--
taux transparents d'un rouge très vif et avec les mêmes caracté--

COTÉ GAUCHE.



COTÉ DROIT.

FOND.

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ristiques optiques que l'Oligiste des fouilles, mêlés à quelques petits morceaux polygonaux comme ceux dant nous pensions, dans - des échantillons antérieurs, qu'ils rappelaient l'ambre moulu.

Les échantillons numéros 9, 12 et 16 correspondent à la couleur gris plomb. Dans le premier, qui est un trait court sur le flanc du "bison barbu", nous trouvons mélangé au pigment une petite particule de ce que nous croyons être de l'ambre moulu.

L'échantillon n°17 correspond à la couleur blanche et contient aussi quelques particules d'hydroxydes de Fer amorphes, - provenant du jaune du fond avec laquelle est très fondue et difficile de différencier.

L'échantillon n° 15 a été pris d'une tache de couleur très violette, que nous trouvons de l'autre côté de la grande crevasse et face à l'entrée dans la salle. C'est un composé organique du couleur carmine dont nous ignorons encore la nature.

Ayant pu approfondir quelque peu la connaissance de ces matériaux de peinture, il reste une série de questions dont nous nous proposons de continuer l'étude.

NOTES.

- (1) Pris de Madariaga B. y Sanemeterio M. "Escritos y Documentos" Santander 1976,pg.15.
- (2) Pris de Cartailhac,E. et Breuil H."La caverne d'Altamira à - Santillane", Monaco 1906, pg. 8.
- (3) Pris de Opus Cit (2)pg.11., (4) Opus Cit (1) pg. 187.
- (5) Opus Cit (2) pg. 6. (6) Breuil y Obermaier "La cueva de Altamira", Madrid,1935, pg.1.
- (7) Pietsch,E. "Altamira y la Prehistoria de la Tecnología Química", Madrid, C.S.I.C. 1964 ,pg.50-51.
- (8) Martí, J. "Informe sobre los estudios realizados en las Cuevas de Altamira", Instituto de Catalisis,C.S.I.C. Madrid 1977.
- (9) Margival F. "Histoire des Techniques de la peinture", en Peintures, Pigments, Vernis, Vol. 35 (1959) pg. 523.
- (10)Opus Cit.(2)pg.259
- (11) En Garcia Guinea,M.A."Santillana y Altamira"Everest,1976,pg64 .
- (12) En Madariaga,B."Hermilio Alcalde del Rio",Santander1972,p.244
- (13) Je remercie leur collaboration à M. Andrés Escalera y M. Antonio Cabllero de l'ICCR et de L'Universite de Madrid respect.
- (14) Lettres du Dr. John S. Mills de 17-X-1977 et 7-XI-1977 contenant un rapport détaillé sur la résine fossile à l'étude.



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ETUDE SUR LA REMISE EN PLACE DE PEINTURES
MURALES DEPOSEES SUR CHASSIS AUTO-PORTANTS
PLANS ET EN FORMES

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5ème Réunion triennale
Zagreb, 1978



ETUDE SUR LA REMISE EN PLACE DE PEINTURES MURALES
DEPOSEES SUR CHASSIS AUTO-PORTANTS PLANS ET EN FORMES

Marie-France de Christen

S O M M A I R E

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- I - Eposé du Problème aboutissant au choix de supports amovibles auto-portants pour la remise en place de peintures murales déposées.
- 2 - Présentation des expériences réalisées transposition et présentation sur chassis auto-portants en résines époxy chargées, de trois fragments de peintures murales.
 - Fragment n° 1 : Surface plane.
 - Fragment n° 2 : Surface mouvementée incurvée en arc
 - Fragment n° 3 : Surface verticale au relief mouvementé.
- 3 - Critique des méthodes exposées :
Limite de ces techniques.
- 4 - Recherches en cours :
à partir de mousses de polyuréthane et de pâtes métalliques, pouvant former des supports rigides et des moules en forme.
- 5 - Conclusion :
Recherches à poursuivre avant la réalisation de grands châssis auto-portants à double courbure de faibles sections (6 à 8 mm).

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I - Exposé du problème :

En milieu humide, le marouflage d'une peinture murale transposée sur un support rigide (bois, mortiers, parlements de pierres), avec, en vue d'une réversibilité, une feuille de polystyrène expansé entre le support et la peinture, ne présente aucune garantie de conservation à longs termes. La colle liant le polystyrène à la peinture est en générale sensible aux micro-organismes, et lors d'une nouvelle dépose, un effritement de la couche picturale serait à craindre, même protégée par des toiles.

Par contre, une remise en place sur chassis auto-portants amovibles permet de transporter sans danger les peintures en cas de nécessité.

Ces chassis doivent répondre à des impératifs techniques précis :

- être composés de matériaux stables et imputrescibles.
 - être rigides en épousant les formes de l'architecture, ou des reliefs de la surface picturale.
 - enfin leur épaisseur doit être limitée à celle de l'enduit, afin de pouvoir, dans certains cas, s'incorporer au niveau d'un ensemble de peintures murales non déposées.
- Dans certains cas, trois à cinq mm. sont requis (ex : peintures exécutées sur un enduit mince sur parements de pierres.

Si le chassis peut répondre à ces qualités, une peinture murale déposée peut se présenter sur place aux regards comme n'ayant jamais été déposée, et, suivant les produits utilisés, être remise en place en milieu humide moyennant une surveillance régulière de sa surface.

2 - Présentation des expériences réalisées.

Les trois exemples que nous présentons ici ont été réalisées sur des petits formats suivant des techniques relativement classiques. Elles ont permis d'étudier dans le détail les différents aspects des problèmes posés et de sélectionner en atelier des matériaux pouvant permettre de d'aborder de plus grandes surfaces.

Fragment n°1 : Peinture plane. (XI ème s. POITIERS, église Saint-Hilaire). 1,90 m x 0,55 m. épaisseur de l'enduit : 6mm - posé sur parements de pierres. Dépose à stacco et transposition au caséinate de chaux (+ acétate de polyvinyle).

Chassis : au revers de la peinture, application d'une feuille de polystyrène expansé (colle employée : acétate de vinyle non plastifié, séché . Fixation à l'alcool à 95° cette méthode évite d'enfermer de l'humidité derrière le

polystyrène expansé de faible porosité. Le support rigide est alors constitué d'une résine époxy à prise lente armée de deux fortes toiles de verre. La dernière couche de résine est imprégnée de sable pour une meilleure présence du châssis. L'épaisseur du châssis atteint 8mm, il est légèrement flexible, et sensiblement plus épais que l'enduit d'origine.

Fragment n°2 :

Peinture incurvée en arc et de surface mouvementée. Ici :
- confection d'un moule en forme de la surface, en vue de la transposition et de la remise en place sur châssis auto-portant. Les dimensions réduites du fragment (1,70 x 0,55 m permettent d'employer une méthode simple : la forme est fabriquée directement sur la peinture, après séchage des toiles apposées en vue de la dépose. La dépose nécessitant des mouvements et une surveillance côté face et revers, le moule doit être détachable et enlevé avant cette opération.

Un ensemble de trois feuilles de papier synthétique adhésif sert de démoulant. Une feuille fut dégagée, permettant la fixation adhésive du deuxième film sur les toiles de dépose. Sur le deuxième film, des bandes de tissu fin pré-enduites de plâtre à prise rapide furent posées en trois épaisseurs. La feuille plastique adhésive a l'avantage de former un écran imperméable évitant toute migration d'humidité vers la fresque à déposer. Une rigidité absolue du moule aurait nécessité une épaisseur de plâtre importante. Pour pallier à cet inconvénient, l'armature fut réalisée par des blocs de polystyrène expansé collés sur le plâtre et découpés dans un plan correspondant à la section de l'arc.

le moule fut facilement détaché du support mural grâce au papier adhésif et servit au transport de la peinture et à sa transposition.

Transposition formant châssis auto-portant. Ici, il ne pas fait usage de toiles et de caséinate de chaux à titre d'essai. Après ammicement de l'enduit d'origine et sa fixation aux résines acryliques, une résine époxy à prise rapide fut directement appliquée sur l'enduit, armée de deux épaisseurs de fortes toiles de verre.

Observations : la section du châssis et de la peinture est ici égale en épaisseur, à celle de l'enduit d'origine. (6 mm). Le châssis est légèrement incurvable, sa rigidité n'est pas absolue, mais suffisante. Il est remis in situ par quelques points d'accrochage de 1 cm 2 en résines époxy avec maintien pendant la prise, directement appliqué sur les parements de pierre. Un solin de chaux relie visuellement la peinture à son mur d'origine.

On pourrait reprocher à cette méthode sa non-réversibilité. Le fragment de peinture ici déposé, ne conservant que quelques traces de peintures, présentait peu d'intérêt. C'est la raison pour laquelle il a été décidé de le remettre en place en milieu humide avec ce procédé, à titre de témoin et d'essai.

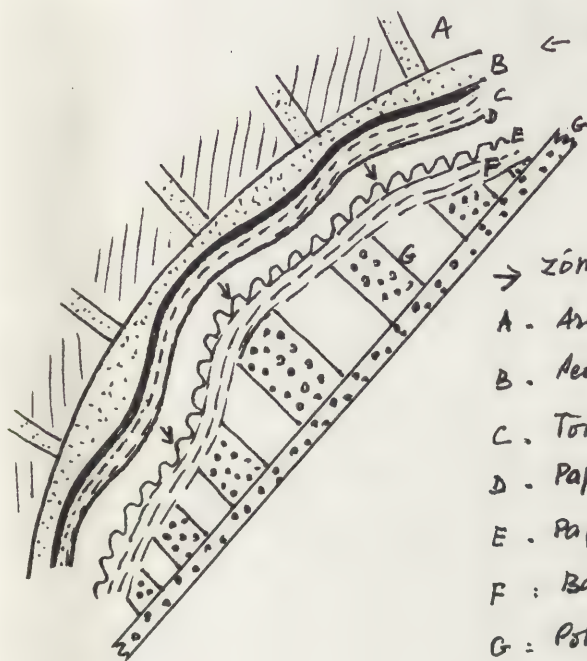
Fragment n°3 :

Surface mouvementée sur plan vertical. (1,20 m x 2,10 m). Peinture pré-romane découverte lors de la dépose d'une peinture murale du XV^{ème} siècle. (Loire. Saint-Romain-le-Puy). Le caractère rare de cette peinture dont la surface présentait un relief très mouvementé a fait opter pour une transposition en forme. La peinture du XV^{ème} s. faisant parti d'un ensemble devant être remise in situ, la dépose, qui se présentait à strappo, était nécessaire. L'humidité du lieu imposait un châssis auto-portant. La dépose devait être réalisée en hiver, par temps humide dans un édifice non clos, de surcroît inaccessible par moyens motorisés. La lenteur de séchage des toiles d'encollage ne permettait pas la prise d'un moule selon la méthode utilisée pour le fragment n°2. La méthode suivante fut adoptée :

- 1 - tracé de lignes verticales parallèles numérotées sur les toiles de dépose. Mise en place, au niveau supérieur et inférieur de deux règles suivant un niveau horizontal et vertical au fil à plomb.
- 2- Découpe de bandes de polystyrène expansé de 2 cm d'épaisseur x 10 cm de largeur x par la hauteur de la peinture.
- 3- tracé du relief sur ces éléments par report en parallélisme (principe du trusquin), et numérotation.
- 4 - Découpe de ces éléments suivant les tracés.
- 5 - Assemblage de ces éléments par collage (colle à prise rapide spéciale pour polystyrène expansé).
- 6- En atelier, ce châssis, formé d'un quadrillage de bandes de polystyrène expansé, fut enduit de bandes de tissu encollées de plâtre, et terminé avec du plâtre à modeler poncé. Une grande précision peut être atteinte lorsque les cotes sont prises sur toute la surface de la peinture avant dépose.

Transposition : toiles encollées au caséinate de chaux + acétate de polyvinyl, puis application d'une feuille de polystyrène expansé de 2 mm de section. L'armature fut réalisée avec une résine epoxy à prise lente chargée de fibres de verre.

Observations : Châssis semi-rigide (mais suffisamment rigide pour être fixé sur un mur) d'une épaisseur variant de 8 à 12 mm (Peinture + polystyrène expansé + résine epoxy).



← Fragment n°2.

- zone de démontage.
- A. Arc en pierres
 - B. Peinture murale
 - C. Toiles de pose
 - D. Papier adhésif
 - E. Papier adhésif gâché
 - F. Bandes plâtres
 - G. Polystyrène expansé.



- A: Mur en moellons
- B: Peinture murale
- C: Règles
- D: Tausquin
- E: Polystyrène expansé
- F: Report du tracé du relief.

← Fragment n°3

3 - CRITIQUE DES METHODES EXPOSEES.

- Sur un moule de surface mouvementée, la transposition au caseinate de chaux + toiles est à éviter, en raison de la tension des toiles au séchage. On peut opter pour deux autres procédés, l'un réversible à base de mousses de polyuréthane, l'autre, non réversible (si ce n'est à l'abrasion) par application directe de résines rigides.

- Le moule en polystyrène expansé peut être utilisé en grandes surfaces verticales, tout en nécessitant un temps de main-d'oeuvre important. Il est exclu pour prendre la forme de voûtes de grandes surfaces à simple ou double courbures.

A noter que la transposition en relief mouvementée ne présente de l'intérêt que pour des peintures situées à peu de hauteur; à partir d'une situation élevée, le relief ne se perçoit pas assez à la vue pour nécessiter une remise en place en forme.

- Les résines époxy armées de fibres de verre utilisées ici ne peuvent être employées en grandes surfaces en raison de leur rigidité insuffisante en faible section.

4 - RECHERCHES EN COURS.

Lors de la réalisation des exemples cités, des essais en atelier nous avaient révélé la possibilité d'utiliser d'autres produits plus adaptés au problème posé, mais nos recherches n'étaient pas assez avancées pour envisager leur emploi.

Deux matériaux ont principalement retenu notre attention.

A - Une mousse de polyuréthane a été expérimentée sur échantillons et sélectionnée parmi d'autres pour sa rigidité et sa qualité moléculaire. Elle peut être utilisée par mélange de deux produits à l'aide d'un agitateur électrique à 18° C. Son emploi exige une grande précision d'action, le temps d'application étant limité à quelques secondes.

Elle est imputrescible, inerte, rigide, totalement réversible, d'une adhérence sur enduits excellente, et peut épouser toutes les formes de surface. Appliquée directement au revers d'une peinture murale déposée (sur enduits fixés), elle constitue un support rigide et stable en une seule opération, évitant tout emploi de colles sensibles aux micro-organismes.

Cette mousse pourrait éventuellement, dans certaines conditions, permettre la fabrication de moules de transposition, utilisée en projection par pistolets spéciaux. Deux sortes de pistolets sont en vente. L'un aisément transportable, sur roulettes, n'est opératif que dans une température de 18°, l'autre, d'un poids de 250 kg, est muni d'un tuyau chauffant, et opératif à toute température.

re. La rareté des dépôts en forme ne permet pas un investissement aussi conséquent.

Enfin la mousse de polyuréthane ici sélectionnée, se trouve soumise à une législation restrictive en France en matière d'emploi dans les lieux publics en raison des gaz nocifs qu'elle dégage en brûlant.

Cependant, son utilisation, qui présente de grands avantages n'est pas à rejeter totalement. Des permis spéciaux peuvent être accordés par les services responsables de la sécurité dans certaines conditions. (ex: peintures en plein air - ou usage restreint par rapport au volume d'air d'un édifice).

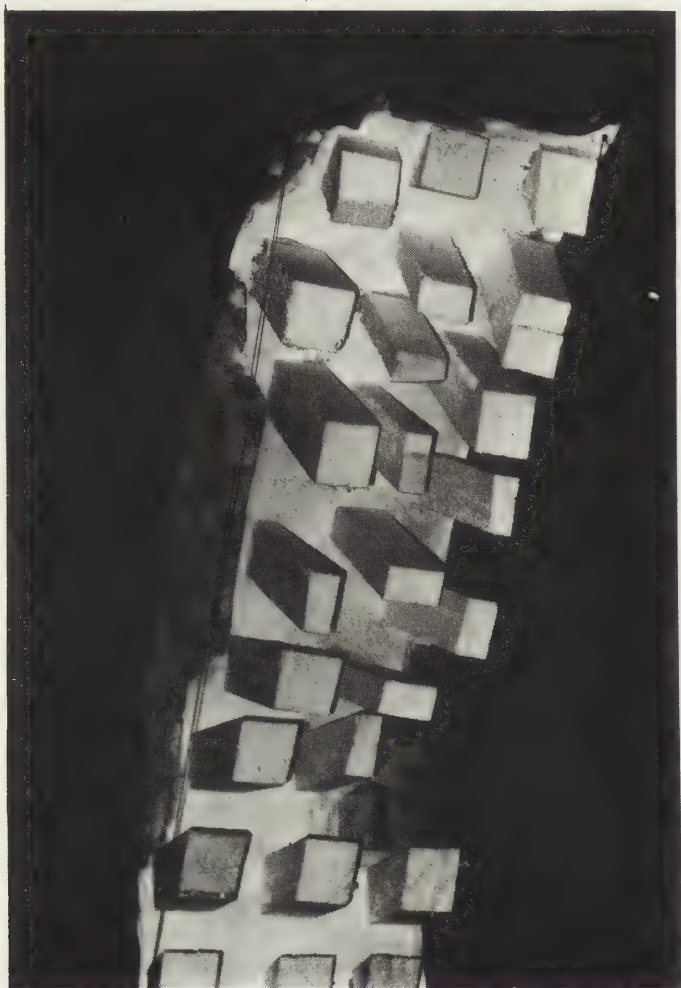
E- Le deuxième produit ayant fait l'objet d'essais en atelier se présente sous la forme d'une pâte métallique à base d'acier, d'aluminium et de chrome qui s'utilise à 18° par mélange de deux pâtes, telles les résines époxy. Elle présente alors, en 2 mm de section, une rigidité absolue sans adjonction d'armature, et remplacerait, sur le plan technique, avantageusement les résines époxy que nous avons utilisées.

Seul son prix prohibitif ne nous a pas permis son usage. (560 frs le Kg par 10 kg en 1975). Malgré ce prix, en fonction même de la simplification du travail et des qualités moléculaires et générales (imputrescible et de conservation donnée comme illimitée) son usage n'est pas à exclure. Dans une température de 18° elle pourrait permettre de fabriquer de vastes moules de voûtes à double courbure, et le moule servir ensuite de châssis auto-portant, un essai ayant confirmé que l'application résine/résine est totalement adhésif.

- CONCLUSION :

D'autres produits et matériaux, pré-sélectionnés, sont en -core à étudier. Il n'est fait ici état que d'étapes sur un sujet complexe : la fabrication de châssis auto-portant à simple ou double courbure, en grandes surfaces. Les solutions peuvent être aussi diverses que les problèmes posés. Il serait souhaitable de pouvoir poursuivre cette recherche limitée et interrompue, faute de moyens.

P.S : Seuls les délais requis pour cette communication nous ont empêchés de fournir les références de tous les produits cités. Elles seront données lors du prochain congrès, si cet exposé peut être fait.



Méthode de fabrication d'un moule en polystyrène
expanse destiné à prendre la forme de la peinture
murale avant dépose.

Méthode employée pour le fragment no. 2.



fragment no. 2:

transposition sur le moule de dépose, après application
de la première couche de résine époxy au revers de la
peinture.



fragment no. 2:

remise en place de la peinture murale transposée en forme.

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BARIUM ALUMINATES FOR THE CONSOLIDATION
OF MURAL PAINTINGS

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5th Triennial Meeting
Zagreb, 1978

BARIUM ALUMINATES FOR THE CONSOLIDATION OF MURAL PAINTINGS

M. Matteini and A. MolesABSTRACT

With regard to the physical and chemical phenomena occurring in the degradation of mural paintings which cause a loss of adhesion and cohesion in the paint layers and lime plasters, consideration has been given to the methods and materials of consolidation. According to Lewyn, Sayre and Ferroni contributions based on the study of mineral bonding products, it is suggested the use of aqueous solutions of Barium Aluminates which should be applied to the painted surfaces. These products should have the double effect of re-establishing the cohesion and of converting the harmful Calcium sulphate into inert Barium sulphate. Moreover these products forming insoluble mineral reaction compounds are more adapted to the materials (plasters) which they have to consolidate.

INTRODUCTION

It is well known that the whole of physical and chemical phenomena, which occur on the surface and in the deeper layers of the mural paintings cause ^{a loss} of adhesion and cohesion of the paint layers and of plasters. These processes varying from time to time according to the work of art, give rise to a precarious and dangerous situation for good conservation.

Among the most important physical and chemical deterioration phenomena, consideration must be given to thermal hygrometric variations, to migration and crystallization of salt solutions, to atmospheric pollution and to microbiological effects.

The so-called "sulphatization" process is perhaps the most diffuse and the one which causes the greatest problems.

Independently of its origin (atmospheric pollution, microbiological effects, presence of sulphurated compounds inside the materials used) the sulphatization finally causes the formation of bivalent calcium sulphate, common gypsum.

This salt, of limited solubility, forms most likely saturated solutions capable of giving crystalline form-

ations which involve not only the surface but also the layers immediately under thus, affecting adhesion and cohesion. (Fig.1)

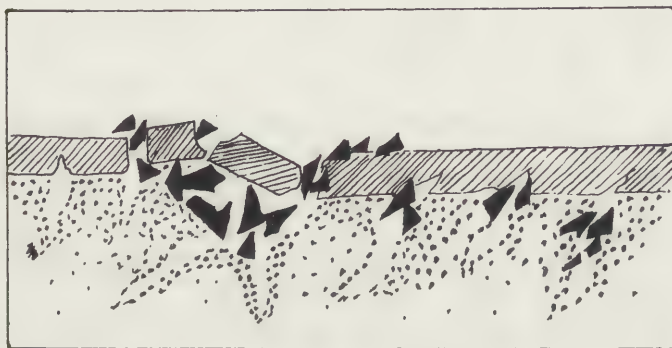





FIG.1

 PAINT LAYER
  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$
  PLASTER

The degradation processes occurring in mural paintings, affects in an analogous but not identical way also stone works.

Today the problem of loss of cohesion is most commonly dealt with by the use of synthetic polymers which, impregnating the surface layers by solution or monomers, would achieve a new cohesion in the treated material by evaporation or polymerization in situ (1. 2.3.)

It must be noted, however, that the results obtained are not always satisfactory. According to different cases, problems arise with the difficulty of penetration, loss of porosity after consolidation, degradation in time (the polymers used being organic materials) irreversibility and above all, partial or total preclusion in possible future treatment by aqueous solutions.

In our laboratories we considered the most opportune choice for consolidating mineral materials, should be oriented towards substances themselves mineral. Researches in this direction date already from the middle of the last century. From this point of view, particularly in the last ten years, Lewyn (4), Sayre

(5,6), Ferroni (7) and others have examined the problem.

The works of these authors point out some fundamental conditions:

- the formation of cohesive compounds must result from gradual time processes.
- the final products must be chemically and physically inert compounds.
- these products should have crystalline and morphological habitus as much as possible similar to the treated material.

Barium hydroxide more than other compounds fulfills the above conditions.

Lewyn and Sayre used above all this compound in the consolidation of stone.

Ferroni's studies, on the other hand, considered Barium hydroxide as an anti-sulphatating agent in fre-scoes.

According to the latter process the polluting Gypsum is converted first into Ammonium sulphate and then the sulphate ion is precipitated by barium hydroxide as insoluble and inert Barium sulphate. Besides excess Barium hydroxide gradually absorbing carbon dioxide re-establishes a partial new cohesion through the formation of Barium carbonate, a compound similar to Calcium carbonate.

Developing these researches in order to improve the consolidating action of Barium and to assure a larger amount of it into the plaster, we decided to study the use of other soluble Barium compounds.

In fact, Barium hydroxide is not very soluble at room temperature (solubility of $\text{Ba(OH)}_2 = .225 \text{ M}$ at 20°C), however the amount in wt. which can be produced in an intonaco, with only one treatment, is somewhat limited but can be sufficient to block the sulphatization.

A synergic action can be obtained by coupling the antisulphatating and consolidating properties of Barium to the cementing action of Aluminium.

This element is known to be the base of the setting of certain cements, through a series of hydrate compounds which have characteristics of insolubility and chemical inertia. To couple the actions of the two elements we tried to synthesize Barium aluminates.

SYNTHESES AND PROPERTIES OF BARIUM ALUMINATES

The synthesis of aluminates can be obtained by a dry method and by a wet method using Barium hydroxide and

Alumina (Al_2O_3) or Aluminium.

a) Synthesis by the wet method

The synthesis using Barium hydroxide and Alumina were eliminated because of the small yield.

Better efficiency results from the exothermic reaction between eighthydrate Barium hydroxide and metallic Aluminium with development of hydrogen.

If Aluminium is used in powder form, complications arise because of the formation of metal foam preventing the reaction.

Better results are obtained by substituting powder Aluminium with Aluminium chips which are anchored to the bottom of the reaction container.

However, by this way, the reaction does not proceed to complete solubilization of the Aluminium.

Many syntheses by the wet method were made using different molar ratios $\text{Ba}(\text{OH})_2 / \text{Al}$.

In table 1 the most significant values obtained on 2 filtrate solutions are shown.

Molar ratio Ba / Al	g.ions Ba^{++} /1000 cc solution at 20°C	g.ions Al^{+++} /1000 cc solution at 20°C
.33	.153	.161
1.00	.226	.216

Table 1

The data obtained show that the maximum amount of "Barium" in solution almost corresponds to the solubility of the Barium hydroxide. At the same time these strongly alkaline solutions contain also a notable amount of "Aluminium" evidently present as aluminate anion.

b) Synthesis by the dry method

At the same time experiments were carried out on the synthesis by the dry method using eighthydrate Barium hydroxide and Alumina.

The choice of suitable temperature conditions presented some problems due to the transformations of Barium hydroxide which occur with increased temperature.

It is essential that the phases come in contact so that at least one of the compounds is present in a liquid state.

On the other hand the melting point of eighthydrate (78°C) is not sufficient to bring about the reaction.

At very high temperatures more than 600°C, Barium peroxides are formed which disturb the yield.

From our experience we found the best temperature is at about 350°C or a little higher.

The reactions were carried out in porcelain containers placed in the oven for about 1 hour at the above temperature. (350°C)

The product of the reaction is a white spongy mass, very hard, which contains a mixture of compounds not all soluble among which we found other than Barium aluminates, alumina and Barium hydroxide which did not react.

The white spongy mass when powdered, treated with water and filtered forms a clear solution strongly alkaline, which absorbs less carbon dioxide than that of Barium hydroxide. It contains soluble Barium and Aluminium as is shown in the following table 2. Also in this case molar ratios of reagents varied.

molar ratio Ba/Al	g.ions Ba ⁺⁺ /1000 cc solution at 20°C (average values)	g.ions Al ⁺⁺⁺ /1000 cc solution at 20°C (average values)
.20	.299	.305
.33	.332	.297
.66	.330	.150
1.00	.343	.151
1.75	.314	.065

Table 2

From the experimental data it is seen that the best conditions of the reaction are those in which molar ratio of synthesis Ba⁺⁺/Al⁺⁺⁺ of 1/3 are used. In these conditions the best result also for the yield of the reaction is obtained. In fact it is possible to obtain about 90% (molar) of the Barium and 32% (molar) of the Aluminium, as soluble products.

Comparing the two types of syntheses, the dry method is preferable to the wet method, because with it, it is possible to obtain aqueous solutions with larger ave-

rage concentrations of the two elements.

It seems also that the average concentrations of Barium in the dry syntheses solutions are higher than those of Barium hydroxide alone. (.32 M against .22 M at 20°C) Correspondingly these solutions contain in addition an amount of Aluminium (a little less than that of Barium) and therefore have potential consolidating properties higher than those of Barium hydroxide alone.

The dry syntheses are preferable to the wet syntheses because in this way we have a solid product in the form of a powder which is more suitable to our method of application. This method consists in applying on mural plaster a wet, short fibered, wood pulp of a special kind containing the consolidant.

This pulp has originally a minimal content of water which cannot be eliminated, without losing the plastic properties necessary for the application. This water could dilute (in the case of wet synthesis products) the concentration of the consolidant, diminishing its efficiency.

This does not occur in products obtained by the dry syntheses which in powder form can be mixed with the wood pulp always giving saturated solutions.

ANALYSES OF THE PRODUCTS OBTAINED

Trials were made to identify the chemical species present in the reaction products.

These analyses were made by I.R. spectrophotometry and by X-ray Diffraction.

Apart from the presence of Barium Hydroxide and Alumina which did not react, we found in the spongy mass many compounds different from these, not always identified, but which contained Barium and Aluminium with an average ratio of 1:1.

From the X-ray graphs, it seemed possible to identify $\text{Ba}_2\text{Al}_2\text{O}_5 \cdot 4\text{-}5\text{H}_2\text{O}$ (ASTM 2-1232). From the I.R. spectra the identification was more difficult.

It seemed that a constant characteristic absorption I.R. band, at about $13.30 - 14.25\mu$, was present.

It is probable that in the solution and in the solid state, there exist a series of Aluminates, with variable composition and hydration, occurring mostly as that mentioned above.

EXPERIMENTAL APPLICATIONS

We experimented on the dry synthesis product obtained at ratio $\text{Ba}^{++} / \text{Al}^{+++} = 1/3$ (indicated AB1) by two different techniques.

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1) A preliminary test was made by immersing samples of old degraded plaster in a saturated solution of the compound AB1 for 24 hours at room temperature.

The samples were taken out, washed quickly in water and left for 2 months in the air.

We made a quantitative control of the Barium on two fractions of the samples extracted from the surface and from the inside.

2) Three parallel tests were made directly on old fresco plaster, by means of applying the solid consolidant mixed with the wood pulp.

a) with 15% $\text{Ba}(\text{OH})_2 \cdot 8 \text{H}_2\text{O}$ solid powder in the wood pulp containing an average of 82% of water.

b) with 8% solid AB1 powder in the same kind of the wood pulp.

c) with 15% Barium hydroxide + 5% metallic Aluminium powder in the same kind of wood pulp.

The applications were maintained on the wall for 2- 3 hours.

Two months later we took out some samples by means of core boring, in the three treated fresco zones and quantitative Barium analyses were made at different depths.

RESULTS

In respect of the plaster samples treated by immersion, it was clearly observed (now only qualitatively) that a significant consolidation and hardening as against the untreated samples, was obtained. At the moment we are carrying out a series of tests in order to obtain quantitative measures of the degree of the obtained consolidation.

To obtain information on cohesion we carried out a special test.

One treated sample and one reference sample were submitted to the action of an equal jet of abrasive powder under pressure (7 atm.) from Airbrasive Jet Machining model K (Pennwalt S.S. White) through a nozzle P/N 353-1847X, during the same time (1m), at the same distance (3cm).

After the test the reference sample not treated with AB1 showed a 2.3% loss of wt. the treated sample instead showed a 1.5% loss of wt.

If these values are representative of cohesion we can deduce that the treatment has increased the cohesion value to about 30%.

It was ^{not} possible to make analogous measures on samples

coming from frescoes because of their small sizes. As a measure of the penetration of consolidants, we referred to the amount of Barium found, against the depth from the surface. These measurements carried out on the frescoes samples show a gradual penetration of Barium with a parallel penetration of Aluminium as we can see in table 3, in the graph (Fig.2) and from X-ray graph in fig.3

treated fresco with	Average distance from the surface in mm.	% of wt. of Ba as BaCO_3 / 100 g. plaster	
Ba(OH)_2	1.25	.79	a
	3.25	.28	
	5.50	.06	
AB1	1.00	.92	b
	3.25	.50	
	5.75	.08	
$\text{Ba(OH)}_2 + \text{Al}$	1.25	.79	c
	3.25	.44	
	5.75	.08	

Table 3

Even with no differences the best results are those resulting from the action of the Aluminates (b and c). We must consider in these two cases that other than Barium, Aluminium also consolidates and that, above all, the AB1 product was used only in 8% concentration against the 15% $\text{Ba(OH)}_2 \cdot 8 \text{H}_2\text{O}$.

PROBABLE CONSOLIDATING MECHANISM

Because of the complexity of chemical species present, it is not possible to define exactly the nature of the processes which beginning with the Aluminates solutions lead to the formation of insoluble consolidating phases. We can however offer a broad hypothesis describing the process.

The solutions we used containing Barium Aluminates and non-reacting soluble Barium hydroxide are alkaline. While by a natural process Barium hydroxide absorbs Carbon dioxide from air converting to BaCO_3 (Barium Carbonate) the PH diminishes and the Aluminates become progressively unstable, beginning a hydrolysis reaction

which converts them to Barium hydroxide and to Aluminium hydroxides.

While the Barium hydroxide continues to absorb Carbon dioxide the Aluminium hydroxides begin to act as cementing substances, with a slow complex mechanism, not exactly clear.

A double cohesive effect gradually results due to both Barium Carbonate and Aluminium different insoluble compounds.

We must consider that the antsulphatating properties of the Barium hydroxide are maintained; moreover Barium Carbonate different from Calcium Carbonate is converted by the action of sulphur atmospheric pollution, to completely insoluble and inert Barium sulphate different from gypsum.

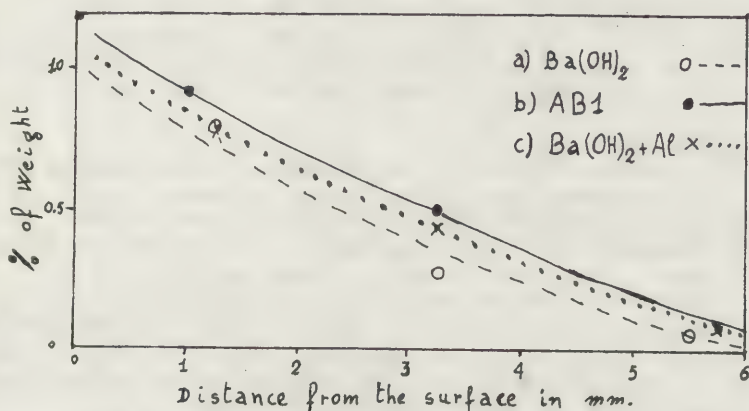


FIG. 2 Distribution in plaster of Ba^{++} as $BaCO_3$

CONCLUSIONS

This work is for the moment merely a proposal of alternative application of consolidants instead of synthetic resins.

The proposal we make based on a valid hypothesis of the action and of the required conditions, has to be verified. Further comparison has to be made with other materials both organic and inorganic in order to fix exactly the limitations and the advantages.

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It is necessary that the practical application of these products on frescoes should be absolutely accurate in the operation. Precautions concerning the possibility of carbon dioxide absorption directly on the paint surfaces which may produce white effects should be taken. We believe this method, especially in relation to future conservation, is more appropriate than the use of other extraneous materials different from those mineral materials present in the fresco plasters. The use of these compounds in the more delicate mural tempera could require more sensitive care. Finally, from these experiments, we would suggest the possible future use of this compound also on stone.

ACKNOWLEDGEMENT

The authors wish to acknowledge Dr. G. Alessandrini of C. N.R. Center "Gino Bozza" in Milan, for her kind collaboration to carry out X-graphs on the samples.

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MURAL PAINTINGS DESALTING

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MURAL PAINTINGS DESALTING

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The work presents two new methods used by INCERC Bucharest for the desalting of the mural paintings as well as, for the extraction of the dust, gudrons, smoke, etc., that often render illisible or destroy the mural paintings.

The advantages of the newly proposed methods are presented in comparison with the classical method of paper pulp - kaolin one.

The two methods are :

- the electrosandwich method based on the negative pressure effect, by the electroosmotic transportation in the sponge layer of the three layers of the device that neighbour the wall;
- the thermal ionizing method for the extraction of salts as well as other impurities; it is based on the moisturing effect of the vapours (ionized or not water aerosoles, according to the case).

R E S U M E

L'étude présente deux nouvelles méthodes appliquées par l'Institut de Recherches dans le Bâtiment de Bucarest, pour la désalinisation des peintures murales ainsi que pour l'extraction des impuretés (poussière), goudrons, fumée, etc., qui parfois rendent intelligibles ce genre d'oeuvres et même les détruisent avec le temps.

On présente les avantages de méthodes proposées en les comparant avec la méthode classique de pâte de papier caolin.

Les deux méthodes sont :

- la méthode de l'électrosandwich qui part de l'effet dépressionnaire du transport électroosmotique vers la couche - éponge attachée au mur, des trois couches du dispositif (fig. 2).
- la méthode thermo-ionisante pour l'extraction des sels et des impuretés adhérentes, se basant sur l'effet émollient des vapeurs (aérosols d'eau ionisés ou non, selon le cas).

1. Report on salinisation of mural paintings

We are aware that the fresco consists in a crust of pseudo-crystalline calcium carbonate incorporating mineral pigments. This crust has a thickness of only some hundredths of a millimeter. This crust appears as a consequence of the rapid carbonatation occurring at the surface of the basic layer of mortar made of calcium hydrate paste (Ca(OH)_2) freshly applied for painting. This layer, in contradistinction with the rest of the plaster, displays an amorphous carbonatation due to its delayed contact with the atmospheric carbon dioxide.

This pseudo-crystalline crust is, of course, a discontinuous one; its surface displays microcrackings, especially at the contact surface between differently coloured zones (due to the different composition and nature of the pigments and their applying technology and especially to the mosaic like structure of the pigment granules); these microcrackings allow the migration to the surface of the saline solutions that invade the building by capillary ascension. This saline humidity, that stabilizes itself at the maximum height (level) (according to the capillary ascension law) migrates towards the walls' outer surface.

The direction of the preferential migration is determined by the maximum thermal and hygric gradient (the law of minimum action), i.e. towards the zones with slightly higher temperature and humidity. Depending on the seasons, these solutions being (inside or outside) close to the surface of the painted walls, concentrate progressively and lose their water by evaporation.

The result of the crystallization of their content in salts has the following consequences :

- produce stains on surfaces turning the paintings illegible;
- deteriorate the pictorial crust by expansive decay caused by the salt recrystallization in the pores of the amorphous calcium carbonate base;
- favour the fixing of biodeterioration agents because the salts in solution constitute a good culture medium for them.

The chemical analyses carried out in the depth of the saline turned walls, have shown that most salts are deposited in the first cm. of thickness (90 %) i.e. especially in the plaster.

For fixing the non extracted soluble salts, B. Bassier (1) recommends the support perfusion with a 1/10,000 solution of double fluo-silicate in water which is a good disinfectant too.

2. Pulp compresses. Method used for saline efflorescences extraction.

The method that is even now used to desalt the mural paintings consists in the application of pulp paste prepared with distilled water on the surface that has to be desalted (2).

These wet compresses laid on the surface that should be desalted, dissolve the salts and, in the drying process, the formed solution migrates into the paste extracting them. This process is repeated for several times.

It is mistaken to mix in the pulp caolin or chalk powder because when drying, they form thin plates which are difficult to extract and when extracting them, they may entrain the weakly fixed pigments (fig. 1).

x
x x

We shall present in the following, two new desalting-cleaning methods, practiced by us, which are more harmless, rapid and efficient.

3. Electrosandwich Method (The method of the electro-osmotic extracting pump)

The mural paintings can be desalted by using this device named in short " electrosandwich " by applying on the surface to be desalted complex compresses that operate by using the electroosmotic phenomenon.

This device consists of three layers of sponge with open pores (for instance polyurethane) or of felt (fig. 2) between which two layers of inoxidable steel or phosphorous bronze grids are laid. The whole so formed " sandwich " is imbibed with distilled or drinking water (depending on the case) and is applied by a slight pressure on the fresco to be desalted (fig. 3).

The electrosandwich outer grid is connected to the negative pole of a continuous current source and the second (inner) grid is connected to the positive pole of the same source. This device operates as follows :

- the sponge (1) covering the wall releases its water to it and dissolves a part of the soluble salts effloresced on the surface;

- the potential difference appearing between the two grids causes an electroosmotic migration of water towards the outside of the middle sponge of the sandwich;

- around the anode, i.e. in the sponge applied on the surface a depression state is caused, which, combined with the usual osmotic tendency of a solution concentrated in salts to migrate in a porous medium towards the solvent by simple osmosis (here the solvent is the water) causes an extraction of the saline solution formed by the dissolution of the effloresced salts;

- the first application of the electrosandwich lasts for 24 hours; then it is dismantled and the 3 sponges are squeezed and washed with distilled water (fig. 4);

- the pH of the squeezed solution is tested for each of the 3 sponges separately; obviously the solution from the sponge 1 is basic, the other ones resulted from the sponge 2 and being acid;

- the successive application of this device is carried out for a number of days until the pH of the squeezed solution is tending to neuter.

The electrosandwich will be built in such a way that the middle sponge (2) should be sufficiently thick (about 4 cm) as to reduce to the minimum possible the water electrolysis effect.

The advantages of our desalting method in comparison to other methods are the following :

- the surface to be desalted is not mechanically affected, considering that the salts are indirectly extracted by a slow electrochemical process;

- the surface to be treated is not chemically affected, because we use for extraction a neuter medium (distilled water) which becomes progressively impure as the salts on the fresco are dissolved in it;

- the salts extraction is uniform, progressive and slow, so that the amount of the osmotic stream formed within the electrosandwich cannot entrain microparticles even if the surface to be desalted is brittle;

- the results are obtained in a shorter interval of time, they are more uniform and they are more sure;

- the desalting influence is felt not only at the surface but also in the depth of the base layer which is also desalted because of the diffusion of the solution formed by water release from the device, which is carried out repeatedly until the solution turns neuter;

- the method can be applied to surfaces of any shape and dimensions;

- the inner processes of capillary migration of the water (saline solution) are, most of the times - reflected in a non-uniform concentration in the porous medium; our method is usable not only for extractions from restrained surfaces but also to repeatings any time it is necessary;

- our method can be also applied to desalt other porous media as for instance the sculptures in stone, due especially to its fundamental quality to take any shape and to act in the profusion of the surface to be desalted.

Concluding, we may characterize the electrosandwich as an aspirating, slow electroosmotic pump.

We shall give in the following actual technical data illustrating the case of the Boyana church (Bulgaria) where this method was applied in 1972.

There, the electrosandwich was applied for five times (1st 24 hrs; 2nd 48 hrs; 3rd 72 hrs; 4th 48 hrs; 5th 48 hrs.).

The subsequent analyses have shown that the extracted salts were the calcium carbonate (dicarbonate) and slight traces of chlorides, sulphates, nitrates (of K, Na, Mg, Ca).

The graphic development of the Boyana application is given by the figures below :

- fig. 5 : the variation in time of the extracted solution pH in the 3 layers of the device
- fig. 6 : the variation of the amount of extracted salts (gr/l) in the 3 layers depending on time;
- fig. 7 : the variation in the electrosandwich depth of the extracted solution pH of the five application;
- fig. 8 : variation of the amount of extracted salts at different applications and in different layers.

Mention should be made that the used tension (continuous current) is of 18 - 21 V.

The currents measured between the different layers or between the 2 poles (the two grids) have decreased in time due to the decrease in the solution conductivity, namely :

- between the poles from 12 - 4 mA
- between the wall and the 1st sponge layer from 0.1 - 0.01 mA
- between the anode and the second layer from 1.25 - 0.1 mA
- between the second layer and the cathode from 1.25 - 0.1 mA.

The electrical resistance between poles, measured before the dismantling of the device, the device being not subjected to tension, varied increasingly from 1.4 - 5 K .

We consider that the solution neutrality is the basic criterion, the other control measurements converging towards it. When this has been

attained the extraction ceased.

Fig. 9 a, 9 b shows the initial and final aspects of the extraction. It should be pointed out that unfortunately nothing has been made to stop the capillary ascension so as it would have been normal.

4. Thermal-electrostatic method (ionized steaming)

Another original procedure of desalting the mural paintings but which is simultaneously applicable to dust, smoke, gudrons, vernis extraction from the painted surfaces, is based on the combined use of steaming (water aerosoles) i.e. of the thermal and dissolving (melting) with the ionization of the same water aerosoles (more or less warm, depending on the nature of the fixed dirt).

Its principle, relies in the heating and electrizing of the surfaces neighbouring that one, that should be cleaned, by electrostatic attraction as supplementary factor leading to the detachment of the fine particles electrostatically fixed or adsorbed by the wall layer (smoke, dust, carbon).

The general case of covering of a surface is with saline efflorescences on which the gudrons resulting from burning, were fixed in a space lattice conglomerated with dust and smoke (carbon particles and gudrons). The more usual dirt is the direct fixing on the painted surface (walls or vaults) of a conglomerate of gudron, dust and carbon. The first adsorbed may be the gudron fixed by sticking, then the dust and the carbon, respect to the oldness of the dirt.

It is true that the dust particles can fix themselves electrostatically, while the gudrons fix themselves by adsorption. Depending on the elements shape and position and on the location of the polluting source, the basic dirt may be first the dust or the gudrons.

In the case of saline efflorescences the forces are larger because they are linked by cohesion to a relatively great depth (1 - 2 mm) in the porous support which is the painting.

Instead, in the case of gudrons fixing, we meet a more complex phenomenon where the linking forces are mainly of adsorption as compared to those of absorption.

In the case of varnishes fixation, the absorption forces in treated porous support are outweighing the adsorption forces.

Thus, our method uses, according to the nature of the fixed dirt, only the electrostatic effect of extraction, or this effect combined with the activating energy entraining the detachment (desorption) by a more or less heating of the water aerosoles (vapours) which are the charge carriers. Thus,

when saline efflorescences are extracted, the steam condensed on the surface has a dissorbing action; when gudrons, varnishes and waxes are disposed off, they have a melting effect.

This treatment is applied (as we can see from the description of the apparatus below) by means of a sponge pad which collects all the impurities of the surface.

The apparatus used by us may have the form of a pistol provided with a reservoir filled with distilled water (fig. 10); its capacity ranges between 250 - 3,000 ml.

This reservoir may be opened at its conical bottom by means of a valve entrained by a trigger; the distilled water flows through a capillary tube which is enwrapped by a spiral electric resistance which heats the water; at its exit the water is turned to vapours. The vapours are directed towards a condenser's armature (plate) which turns the fine water particles into electrized aerosoles. Then, these aerosoles pass through a sponge or glass fibres felt pad.

For a maximum protection of the surface to be electrostatically cleaned, the sponge pad is kept at 1 - 1.5 mm distance from the wall by means of a brush with rigid-elastic wires which surround the sponge.

The active surface of the sponge can vary between 200 - 2,000 sq.cm. The aerosoles are pumped at intervals of 3 - 5 seconds and the thickness of the sponge pad varies between 5 - 12 mm. At the beginning the sponge may be used for about 1 minute (i.e. about 10 - 20 successive applyings) then it should be replaced by a clean one.

The advantages of this method in comparison to other similar ones are the following :

- it does not influence in any way, either mechanically or chemically the surface to be treated;
- in case of removing marine efflorescences which adhere stronger, the activating energy of the utilized jet of vapours which is attenuated by the collecting sponge is enough to dissolve the fixed salts, even the insoluble carbonates; by the absorption effect of the sponge pressed on the surface, the solution formed by condensation migrates in the sponge and causes the extraction;
- we can be sure the no altering thermal effects occur, because the heat losses of the vapours formed by the electrical resistance on the treated surface, are very high;
- our method is in fact a combination of the electrostatic and thermal ones, and uses electrized vapours of distilled water

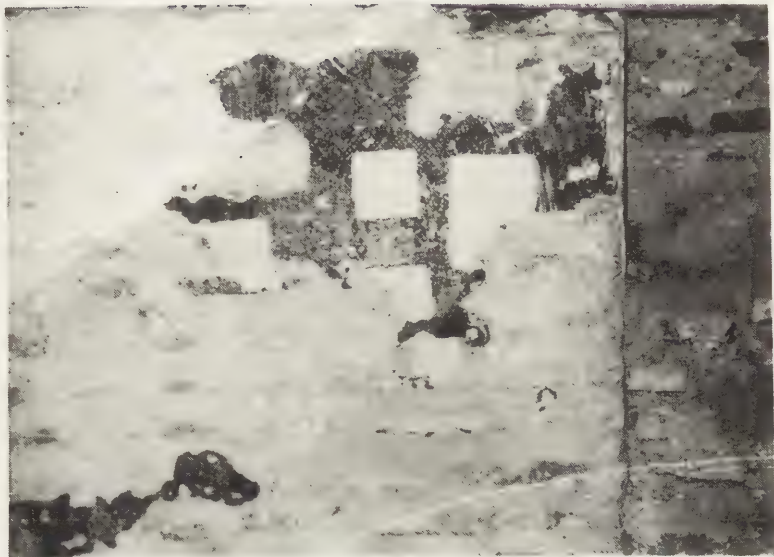
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(aerosoles), i.e. independent, out-distanced and impossibly contingent microparticles, as they are all charged with the same electrical charge; the passing through the electrically insulating sponge is occurring by its charging by electrostatic influence, i.e. no charge loss or recombination take place.

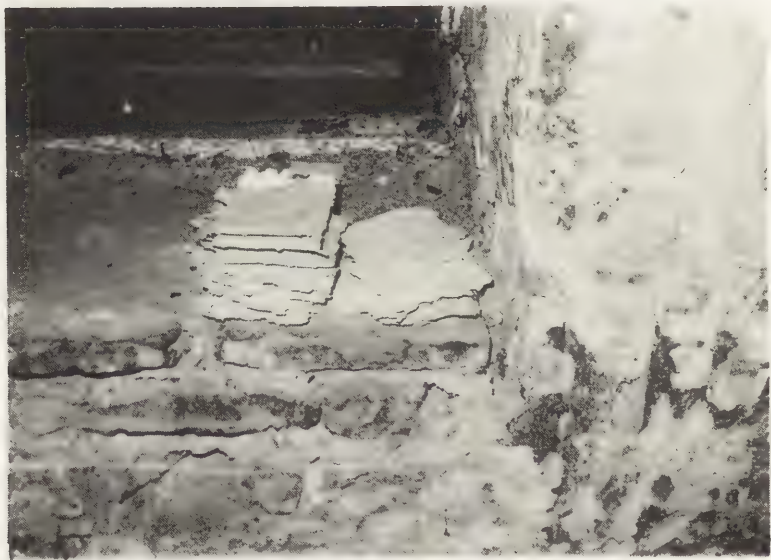
Fig. 11 presents some instances of applying this method.

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1 a



1 b

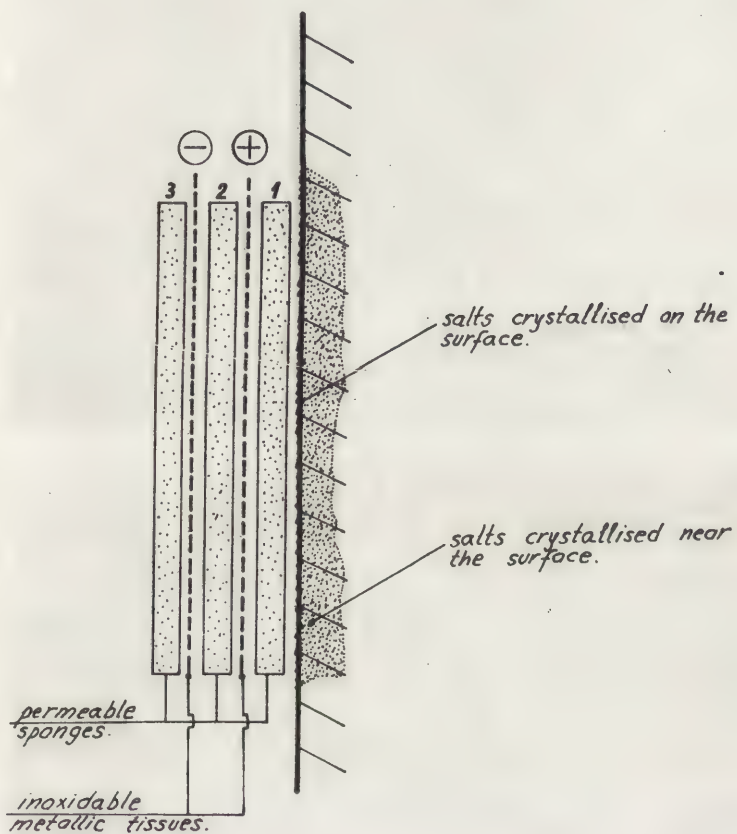
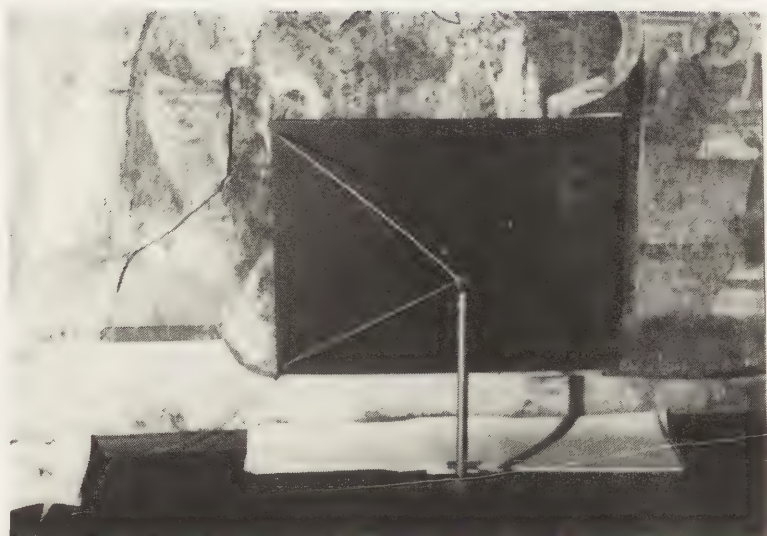


FIG. 2

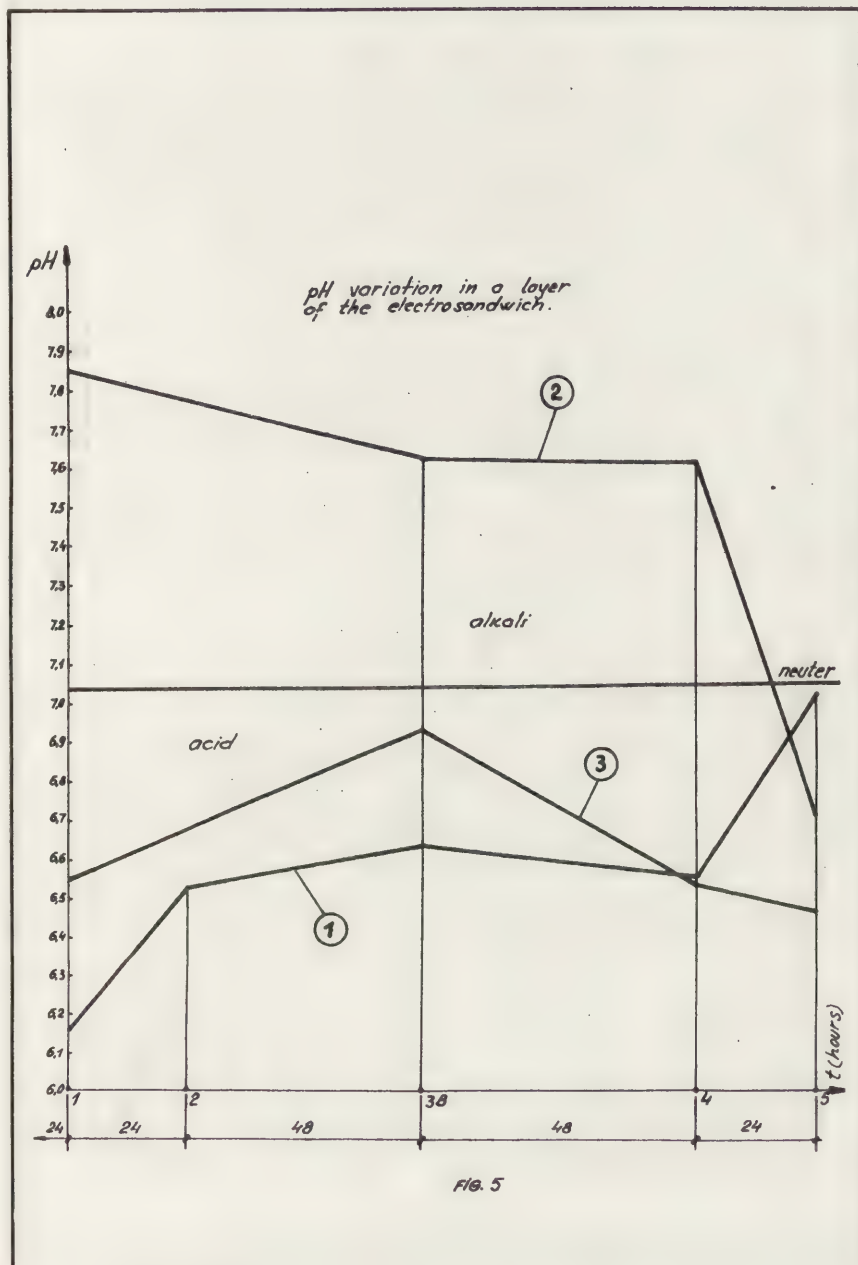
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3



4



Cumulated variation of the extraction of salts in the three layers of the electro sand wich.

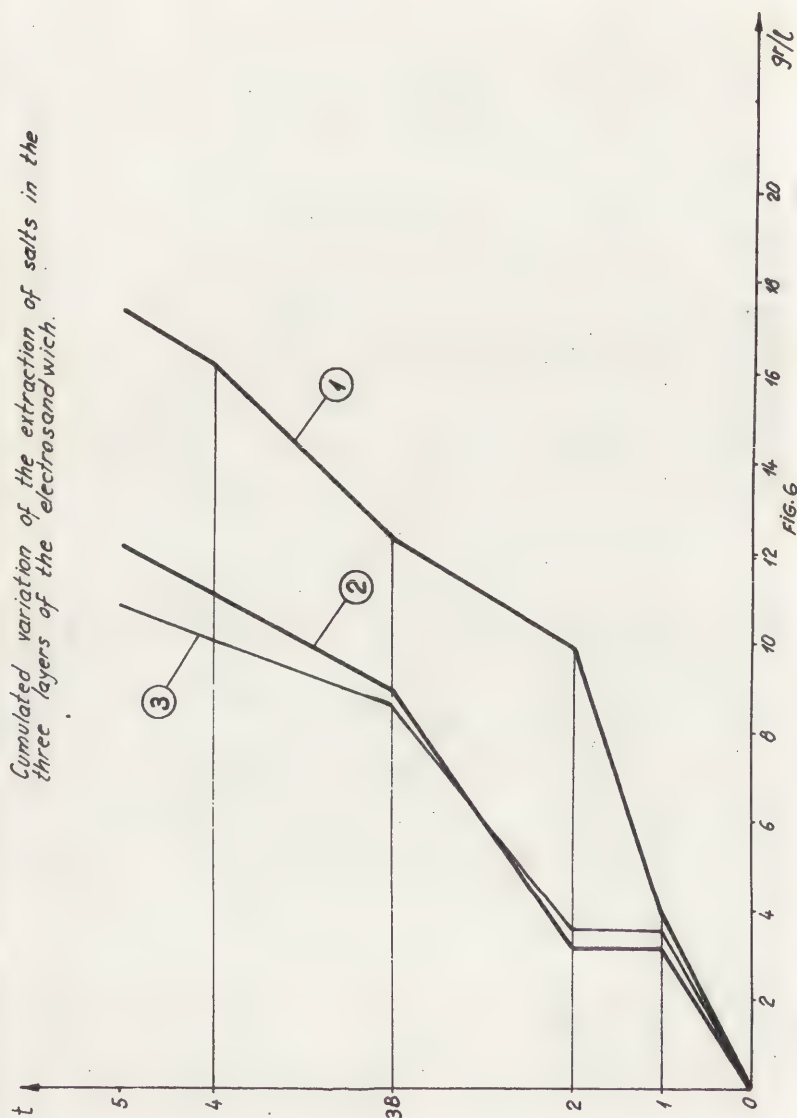


FIG. 6

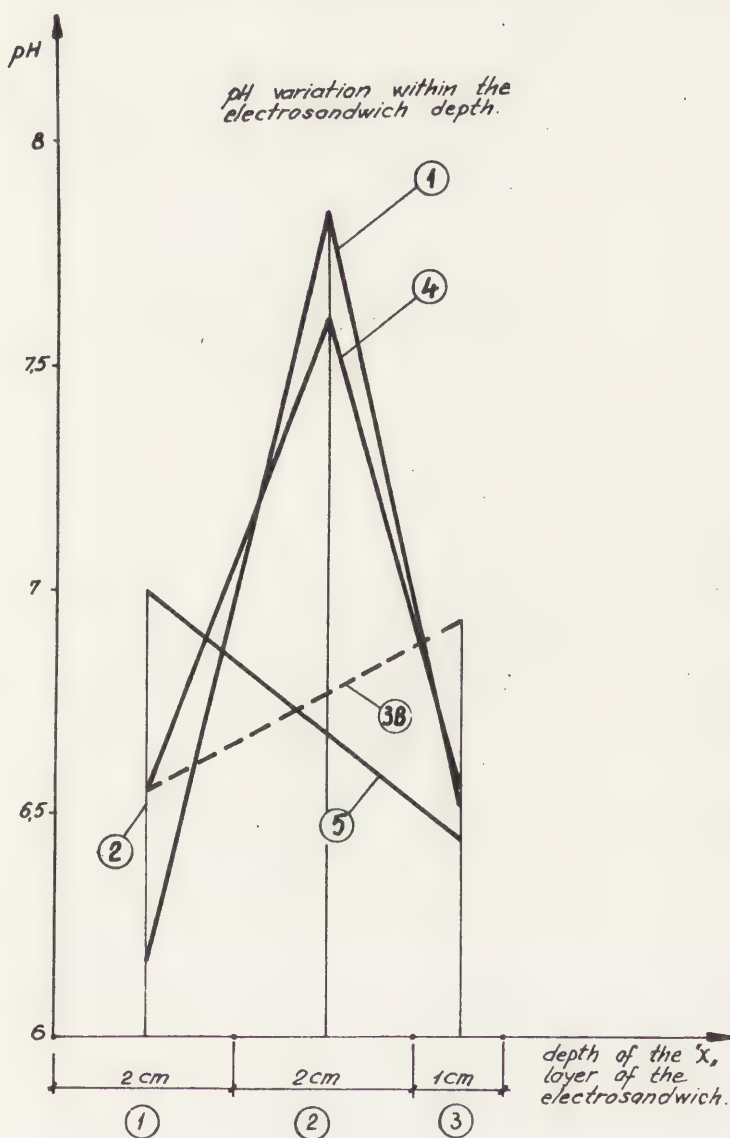


FIG. 7

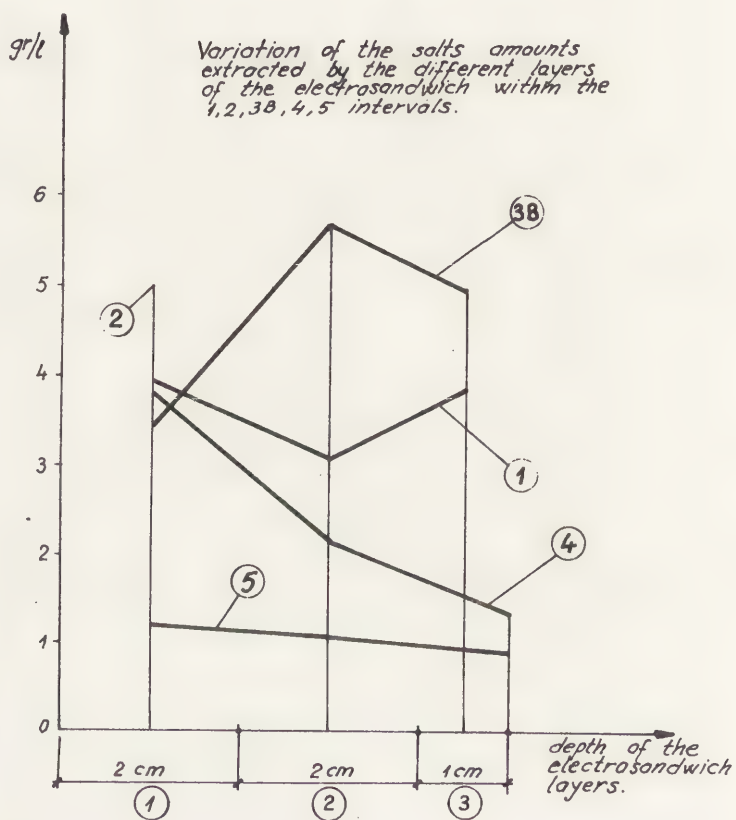
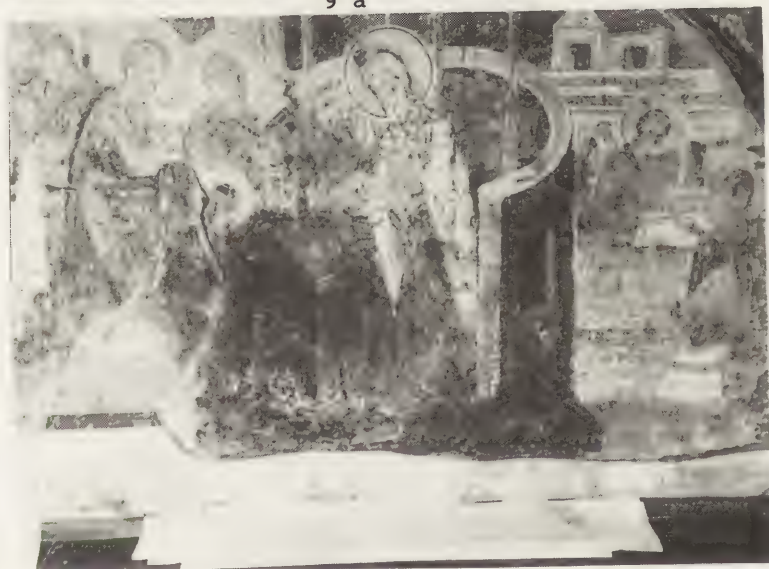


FIG. 8



9 a



9 b

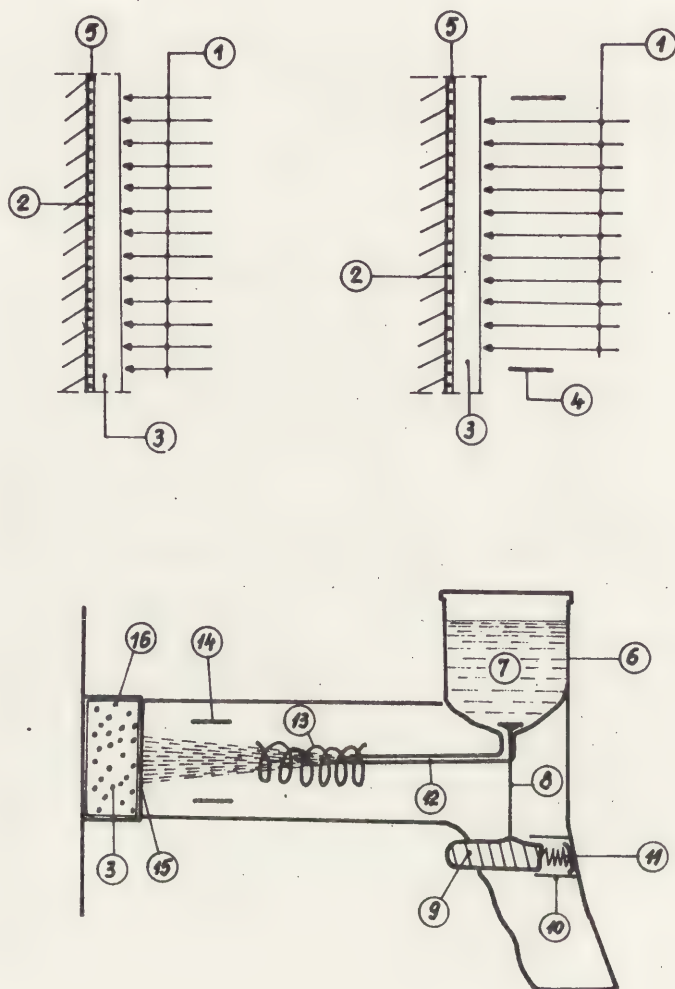
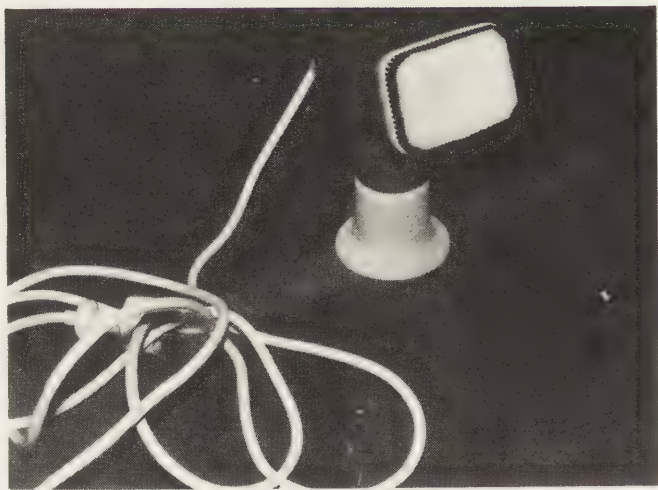


Fig. 10

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11 a



11 b



11 c



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THE CONSERVATION OF ADOBE WALLS
DECORATED WITH MURAL PAINTINGS AND
RELIEFS IN PERU

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ICOM Committee for Conservation
5th Triennial Meeting
Zagreb, 1978



THE CONSERVATION OF ADOBE WALLS DECORATED WITH MURAL
PAINTINGS AND RELIEFS IN PERU

Zoltán Szabó

Abstract - The buildings decorated with wall paintings and reliefs were made of adobe on the narrow costal desert of Peru. Both the excavated original parts of the buildings, and the completed ones are equally deteriorated by the wind and the rare but strong rains. For the building material of the completed parts the author suggests an adobe tempered with 10 v/v % of lime cream, which has become waterproof. The original parts could be protected by poly-acrylates or polystyrene procurable as cheap industrial wastage, too.

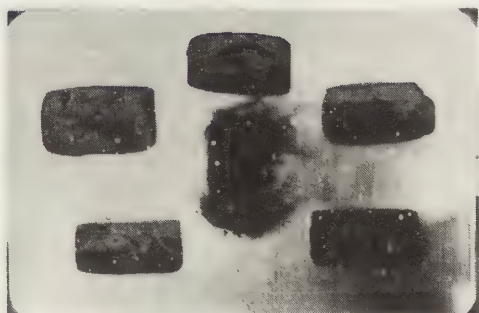
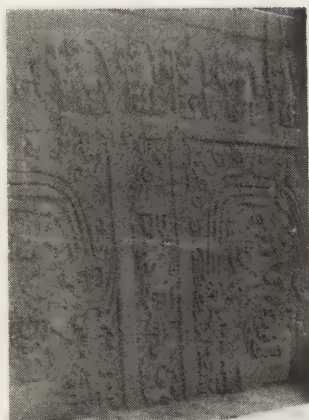
The adobe, as building material, was used in Europe mostly in the rural architecture. In the European climate the adobe is a more efemer material than the stone or the brick. But in the Peruvian climate the adobe is durable, because on the seaside of the Pacific ocean, owing to the cooling effect of the Humboldt Current, there is a nearly 3000 km long desert, where the random of the annual rainfall is between 0,025 and 50 mm pro year. The distribution of the rainfall is very extreme: in every 20 years there is a strong tropical rain-storm and between the rain-storms only the fog moistens the desert. The bulk of the people was settled in this costal desert. The big costal kingdoms based on the irrigating system of the agriculture were developed here. Their golden age was between the twelfth and the fifteenth century A. D. They fell victim to the highlanders' conquest /the Inca empire/.

The most powerful kingdom was the Chimu empire. Its capital, Chan-Chan was built on about 18 km² and had about 100.000 inhabitants. This was the biggest city of the pre-Columbian America. The walls of the town, the artificial hills of the temples, the palaces, the houses etc. all were built completely of adobe. The walls of the important buildings were decorated with reliefs of adobe /Fig. 1/. Even the support of the paintings in the fortresses and sanctuaries was adobe. All the towns of the arid seashore were constructed in the same way.

As long as the buildings were used, the damaged reliefs and paintings were repaired by the inhabitants in every 20 years after the rains occurring periodically. Therefore the paintings are consisted of many layers. After the Inca conquest the ruler class was partially exterminated, the craftsmen were settled in Cuzco or near to the lake Titicaca, and many towns became depopulated. The Spanish conquerors found only the ruins of the towns. In the last five centuries the rain washed down the upper part of the walls, and this debris protected the remains of the wall. After this protective cover of debris has been cleared away by the archaeological exploration, the wind, the sunshine and the rare but strong tropical rains deteriorate the town, the original walls /Fig. 2/ and the completed walls /Fig. 3/, too.

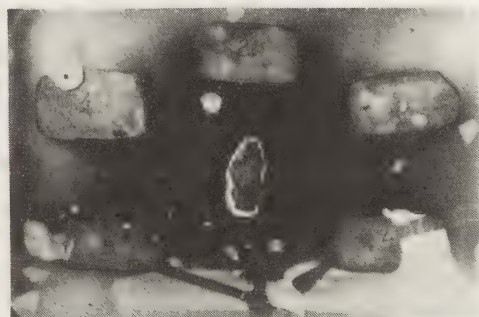
To the request of the Centro de Investigación y Restauración de Bienes Monumentales of Peru the method for the conservation of the adobe of the Hungarian popular architecture was adapted to the conservation of the Peruvian buildings.

The adobe of the ruins of Garagay was used for the experiments. This archaeological site is near to Lima, and it is a very important task to protect the polychrome painting representing animals, which decorate the walls of the sanctuary. We have two problems to solve: partly to elabo-



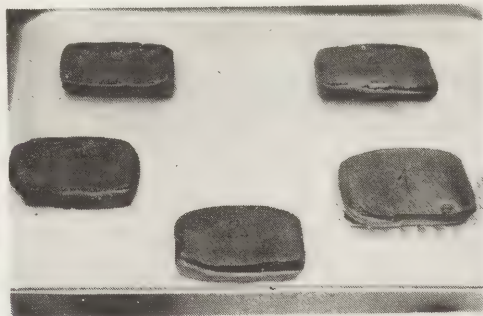
▲
FIG. 4

◀ FIG. 1



▲
FIG. 5

◀ FIG. 2



▲
FIG. 6

◀ FIG. 3

rate a modified, waterproof adobe used for the completed new parts of the walls, partly to conserve the original surfaces using an adequate protecting coating. First of all the contraction of the drying adobe was determined. We have drawn three 25 cm long lines on the surface of the freshly prepared wet brick. After two days of drying their lengths were 24,7, 24,6 and 24,7 cm correspondingly. The contraction was only 1,3 %, which was less, than the 2 % limit value. Under 2 % of contraction it could be modified with lime without tempering with anorganic or organic filler /sand or straw/. So we didn't have to temper the adobe of Garagay before using it for the experiments.

Lime cream in 20:6, 20:4, 20:3, 20:2 and 20:1 volume proportion was given to the dry adobe. It was pugged by adding some water until it became easy to shape little bricks.

The bricks of adobe mixed with lime have been dried on the open air for a week, then they were dipped into the water with a brick shaped of adobe without lime. The brick of adobe in the moment of dipping began to dissolve /Fig. 4/, and in 10 minutes lost its shape and disintegrated /Fig. 5/. The bricks made of adobe mixed with lime have remained unchangeable under water for days, even for months /Fig. 6/.

The colour of the bricks containing lime was some brighter, than the colour of the original adobe. All the five bricks were waterproof, but the bricks made after the first four proportions had required mechanical properties, and the bricks made after the last two proportions had the most proper colour. Therefore the 20:2 proportion /10 v/v % of lime cream/ is suggested to be used for completing the walls.

In the second part of the experiments some bricks of adobe were shaped by means of a wooden frame, and they

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were dried until they were in a state of equilibrium with the water content of the air. Then the bricks were covered with a solution of synthetic polymers made with organic solvents. These materials were synthetic lacquers proved good for conservation or cheap industrial wastage obtainable in Peru. We wanted to prove, if they were proper for the consolidation of adobe. The bricks were tested by two respects: /1/ how the original colour and appearance of adobe remain after the covering, and /2/ has the covered surface become hydrophobe or not? On the picture /Fig. 7/ you can see at the left the covered surface, and at the right the uncovered one ten seconds after dropping it with water.

Results

I. Bedacryl 122-X. The original poly-n-buthyl-metacrylate solution was diluted to 1 %, 2 % and 5 % with aromatic solvents. There was not any difference between the benzene, toluene and xylene, but the solution made with benzene absorbs and evaporates more rapidly than the other. The 1 % and 2 % solution of Bedacryl didn't change the colour of the adobe, but the 5 % solution darkens it. The Bedacryl made the adobe perfectly hydrophobic in all dilution.

II. Paraloid B-72. The 1 %, 2 % and 5 % of the methyl-metacrylate and aethyl-acrylate copolymer in xylene made the surface of adobe completely hydrophobic, but didn't change its colour or appearance.

III. Paraloid B-82. This copolymer was less effective, than the Paraloid B-72. The 1 % and 2 % Paraloid B-82 solutions don't change the colour of adobe, but the 5 % solution darkens it.

IV. Nowilith 50. The poly-vinilacetate was dissolved in 1:1 mixture of acetone and ethyl-alcohole. It makes the

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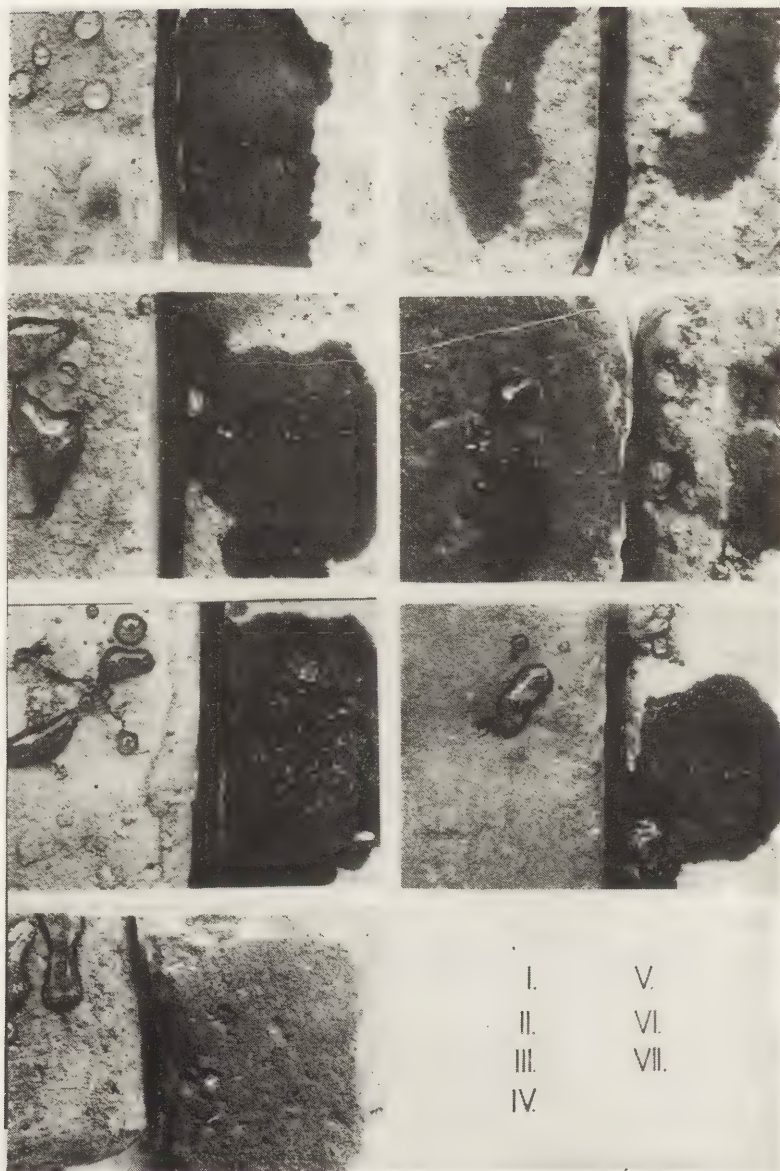


FIG. 7

surface hydrophobic, but darkens the adobe in all the three concentrations.

V. Mowiol 18-80. This poly-vinylalcohol with high acetate content is dissolvable completely only in water. It discolours the surface and doesn't make it hydrophobic. It is not effective for this purpose.

VI. Calaton CB. The Nylon derivate dissolves only in water containing aethyl-alcohol. It doesn't make the surface hydrophobic, so it cannot be used for this purpose.

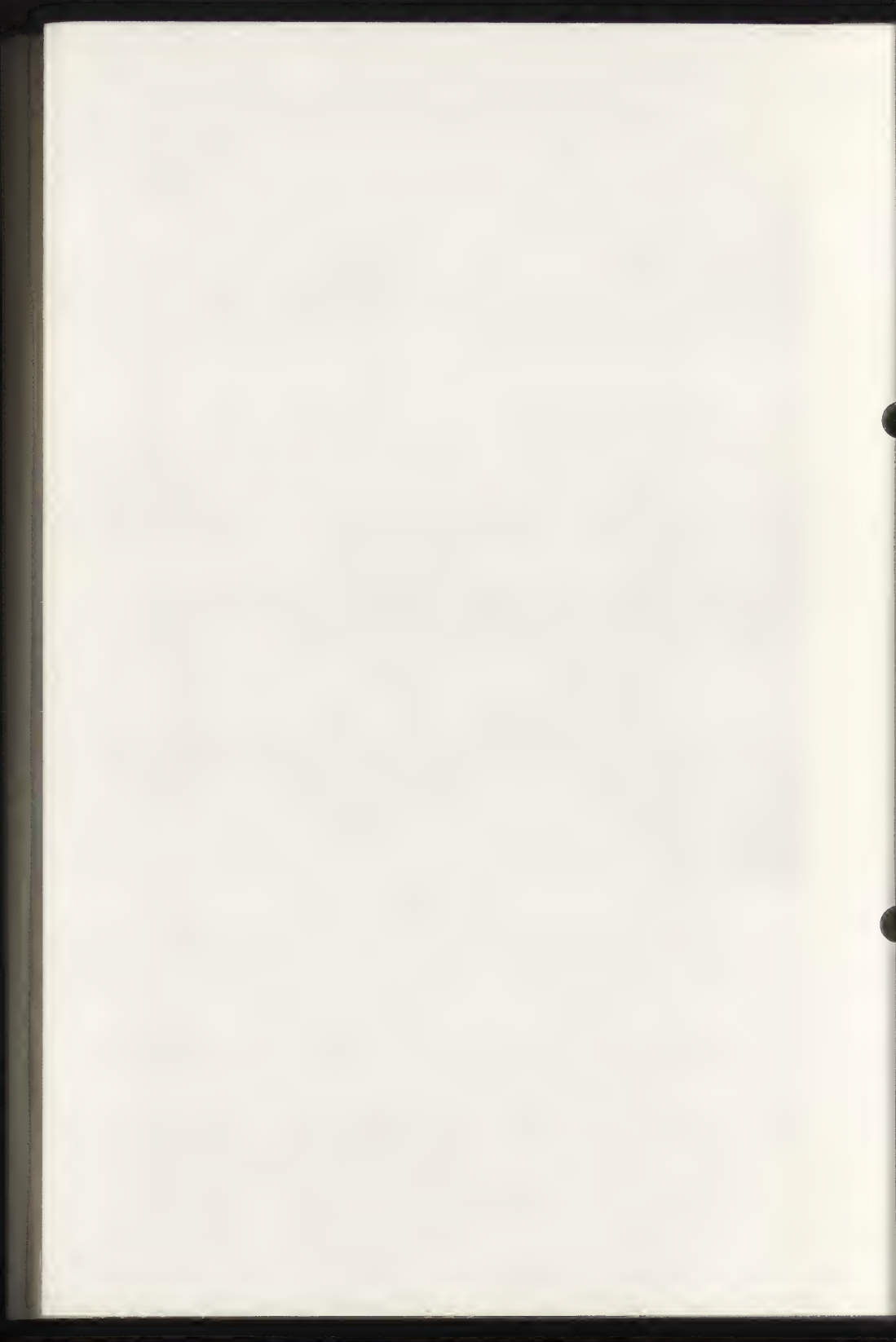
VII. Polystyrene. The solution of 5 % polystyrene in xylene made the surface completely hydrophobic, but it didn't change its colour.

To sum it up, for the conservation of the original adobe walls the acrylate and metacrylate derivatives and the polystyrene seem to be the best. All these materials occur as industrial wastage, too. By using them we could conserve large surfaces at small cost.

It is only a possibility for the conservation of the adobe walls. I didn't have the opportunity to try it on the Peruvian monuments, but I suppose on the basis of the Hungarian experiences, it would be effective on the Peruvian buildings, too.

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A FEW PROBLEMS INVOLVED IN THE
CONSERVATION AND VALORIZATION
OF MOSAICS

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Zagreb, 1978



A FEW PROBLEMS INVOLVED IN THE CONSERVATION AND VALORIZATION OF MOSAICS

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Mosaics are to be allotted an outstanding role among stone works, although their formal structure may not entirely consist of lithoid material, i.e. of quarry stones or pebbles; in works extant within the area of Greek-Roman civilization such material is in fact often supplemented with either glassy matter (glaze) or any other material of a different nature (for instance bricks), supported and connected by mortar.

Today a wealth of problems are involved in the preservation of mosaics - most of which are exposed to the open air. - They include numerous and complex stages among which basically those connected with the description of their characteristic features and with suitable methods of intervention (the latter were debated of late in the "First International Symposium on the Preservation of Mosaics" (°) sponsored by ICCROM in Rome in Novembre 1977), as well as those of using mosaics to advantage, allowing them to be enjoyed both in situ and in museums.

All these stages call for ever more refined scientific aids - sometimes even completely new ones - whether one has to safeguard works located in archaeological sites and mediaeval buildings, or when works of art come to light owing to archaeological excavations or urgent edification or road works. Such works of art are to be given a suitable arrangement and destination within enclosed places.

It will be useful to emphasize here the fact that although this particular expression of art has been extensively dealt with in historical and philological literature, its scientific as well as operative aspects have been quite neglected, so far, by scientific research, inasmuch as traditional intervention techniques are still found in use side by side with more advanced technological procedures, whose experimental aspects and application, by the way, are constantly evolving. It is moreover neglected by society as a whole, which generally ignores its basic aspects and historical as well as territorial worth.

And now, as I turn to the problems involved in preserving mosaics and turning them to account, may I mention some of their characteristic technical aspects as well as the scientific methods suitable to define their basic features, i.e. to ascertain their genesis, physical structure and historical vitality within their environmental, architectural or territorial setting. Only from such all-inclusive knowledge, aided by research on the spot, as well as by experience and means - either already well-known or at least in an advanced stage of experimentation - there may spring a methodology capable of working out suitable preserving interventions and making due allowances for the main causes of their deterioration. As regards the latter, we must mention, besides ageing, the indirect action of traffic (both air and vehicular), wearing through feet-stamping, ambient humidity, spontaneous flora and the action of microorganisms and, last but not least, causes of a social nature, i.e. negligence.

Causes which are often present and detectable within one and the same mosaic but have not been all of them sufficiently investigated either in their reciprocal relationship or with an eye to possible preservation methods, among which removal of the work and transfer to a museum is by now becoming the prevailing practice.

Owing to some historical facets and events pertaining to the evolution of this artistic expression, mosaics have been included in the vast genre of painting; Domenico Ghirlandaio's (1449-1494) well-known saying that the mosaic is to be considered as "the real painting of eternity" is particularly grounded in the - unfortunately no more than apparent - durability of the peculiar materials it is made from.

Here is the convincement which has so far accounted for the adoption of restoration methods similar to those in use for paintings either on wood or on canvas, as well as for their custody within museums, where even floor mosaics are exhibited in frames, hanging from the walls.

It will be useful to remember, in this connection, that from the 19th century onwards there has also constantly evolved the method of re-use, i.e. of displaying mosaic compages in museums on the floor, where they form the new flooring of the rooms.

Either method has been extensively used for the mosaics, found in Pompeii and Herculaneum, that have been exhibited in the Naples Archaeological Museum since the 19th century; the floor mosaic with the "battle of Alexander" (m.5'35 x 3'16, restored by the mosaicist Belliagzi in 1941), is set on the wall and so are other, though smaller and less famous works. As is known, this mosaic was found in the house of the Faun in 1831 and transferred to Naples in 1843. Other mosaic compages are to be found on the floor in some of the rooms of the Naples Museum, perverting the aesthetic, historical and architectural worth of that building with a medley of images and spaces. Similar examples can be found also in other museums, both in Italy and abroad.

It is time, by now, for such methods to be definitely abandoned, although also the problems connected with alternative methods are quite complex. No doubt the relationship between mosaics and museums is at this stage to tally unexplored and must be investigated with an eye to the possibility of reconciling exhibition with preservation whenever there is the absolute need of keeping works in museums or other enclosed places, and at the same time of safeguarding not only their semantic, but also technical and tectonic worth. It will suffice to remember here that the latter is based on the proportional correspondence of the single element (tessera) with the whole composition and the room where it is to be placed.

Such are the principles that must underlie the planning of architectural patterns fit to contain mosaics, and therefore the selection of museological patterns capable of bringing about a new relation between the observer and the object of art in its container. They are in fact referred to in the recommendations forming paragraph C of art. 5 in the UNESCO Convention of 14 Nov. 1970 regarding one aspect of the safeguarding of our cultural heritage. The member states' conviction is such as to result in their commitment in "promoting the establishment and expansion of scientific and technical institutions (museums, archives, laboratories, etc.) capable of warranting the preservation and better utilization of our cultural heritage.

As I said before, it is my aim to lay stress only on a few of the numerous problems involved, i.e. the technical and tectonic ones; therefore I deem it useful to make

two preliminary remarks which, referred to a typical operative example, justify the adoption of a particular technique - photogrammetrical survey - capable of satisfying, in my opinion, both the needs of the preliminary documentary stage and those of subsequent preservation.

My first remark is referred to the technical characteristics of mosaics.

Viewed as paintings, mosaics display some analogy with frescoes: either wall decoration type is supported by plaster on whose uppermost, still fresh layer the chromatic texture is placed. In frescoes the latter is made up of tiny, water-suspended mineral particles, spread on with the brush; in mosaics a coarse-grained natural or artificial material is arranged on it by hand. From this point of view the two chromatic textures show remarkable similarity: the microaspects of the former are matched by the macrodimensions of the latter; but their results, on the contrary, are dissimilar both from a technical and an expressive point of view. Such unlikeness accounts for the use of different preserving techniques.

The tessera is therefore the central element in the mosaic structure: it objectifies the design and, through the medium of its supporting plaster, comes to life on wall structures, whether horizontal, vertical or curved, entering a vital and indissoluble relationship with them. In particular, if the tessera is considered in its material individuality and semantic structure, it becomes the element through which the unity of a composition is expressed: its shape, size and colour contribute to determine the stylistic characteristics of the cartoon, and so does the other element also partaking in the composition, i.e. the reticular texture, the weftage formed by the little stones and the underlying connecting mortar. The above-mentioned elements determine such unitary aesthetic results as make mosaics appear entirely different from paintings, from which they differ also owing to their utilitarian and ornamental functions, based on the role performed by mosaics, as well as walls and ceilings, as integral parts of the architectural structure. Such aspects are found to be typical of the productive trend which developed in Italy and the Latin provinces between Greek-Roman times and the Byzantine era.

My second remark concerns the creation of a detailed

inventory for the protection of this expression of art. Among necessary systematic operations I would include a catalogue of our mosaic wealth wherein to certify the physical characteristics, historical outline, iconographic description, date and state of preservation of the single works, also with reference to the fabrics where they are lodged according to the author's design.

The description of each work should include its constituent materials, information about the architectural structure and geographic as well as environmental peculiarities of the place where it is located, together with those of the original site as well, in case the mosaic has been moved. Particular care ought to be devoted to the search for possible mosaic drawings, i.e. sinopie and cartoons, mostly kept in places other than those of the works whose planning phase they bear witness of.

At this stage, in order to point out one of the numerous problems relevant to the preservation of mosaics, whether they are to remain in situ or to be moved elsewhere and displayed in an enclosed place, I shall give details about a mosaic floor which, having been treated more recently (1973-74), may prove exemplary both because of the reasons of its decay and the type of preserving work done on it with the aim of safeguarding the mosaic as a whole and allowing it to be used to advantage.

The technical and expressive peculiarities of this mosaic - which can be found in other documents as well - were clearly revealed by a floor fragment found in the tablinum of a large colonnaded "villa" in the residential city of Stabiae, on Varano upland plain. As its former owner has not been identified, the house has been marked "A" for the time being. The tablinum and other rooms rest on the utmost verge of the upland plain, with landslips below. The subsidence connected with such position, having already caused the crumbling of the mosaic structure in the past, was threatening to destroy the remaining parts as well. The remains were therefore detached (by the Naples and Caserta Superintendency staffs), to be replaced on the same spot later, after due restoration of the work itself and the necessary reinforcement of the subsidence-prone ground.

The mosaic-finds (°°) include parts of the external, geometrical decoration, with portions of the central area and a large fragment of the sinopia; a fact which appears of outstanding historical interest, being unique

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in Campanian archaeology. The sinopia came to light on the second layer of the mosaic, which had been smoothed with a straightedge, and consists of a grid of lines cut in the plaster itself, and of a superimposed geometrical pattern outlined with the brush soaked with a water solution of coal dust.

It will be apt to remember here that this unique Campanian find is matched by the discovery of a sinopia on the occasion of systematic archaeological excavations in the Roman city of Utica, Tunisia. The graphic find is analogous with that of Stabiae both on account of its planning technique and the method used by the antique mosaicist for work on it.

The study of this Stabian floor with reference to the extant wall remains has led to the reconstruction of the preliminary drawing, while laboratory research on some of its fragments have allowed to ascertain some elements of the building technique used in Roman times. In fact the mosaic dates back to that age (middle of the 1st century A.D.) both on account of its composition scheme and the building technique of the walls enclosing it.

The materials it is made from are white and black. The former is limestone of a compact, microcrystalline structure, easily found in the "Agro campano"; the latter is of a lavic nature, being drawn from leucitic rock of a micromeric structure not to be found on the spot, i.e. on Vesuvius - Mount Somma. It is very much like the lava of the Roman plain, characterized by such uniformity of the constituent mineral elements as makes it more suitable to neat cutting into tesserae. The same would not be possible using phenocrystals, of which Vesuvian lava is made. The use of leucitic rock bears further evidence of cultural contacts between Rome and Stabiae also in the field of artisanship.

From what I have shortly outlined before there emerges clearly that while the first operations both in situ and in laboratories have allowed to bring to light the different constituent layers of the work and to determine its peculiar technical and cultural features, the problems connected with preserving the work itself and its sinopia had not been touched upon yet. The sinopia being prone to decay if left in the open air, must be protected in a particular way, i.e. enclosed in a suitable container with transparent external surfaces, and must also be displayed beside the mosaic which is based

on it. The question remains open whether the mosaic must be re-placed in situ or moved to a museum. At this point I mean a museum (located within the archaeological area or the architectural complex), one section of which should be specially planned and destined to the exhibition of mosaics.

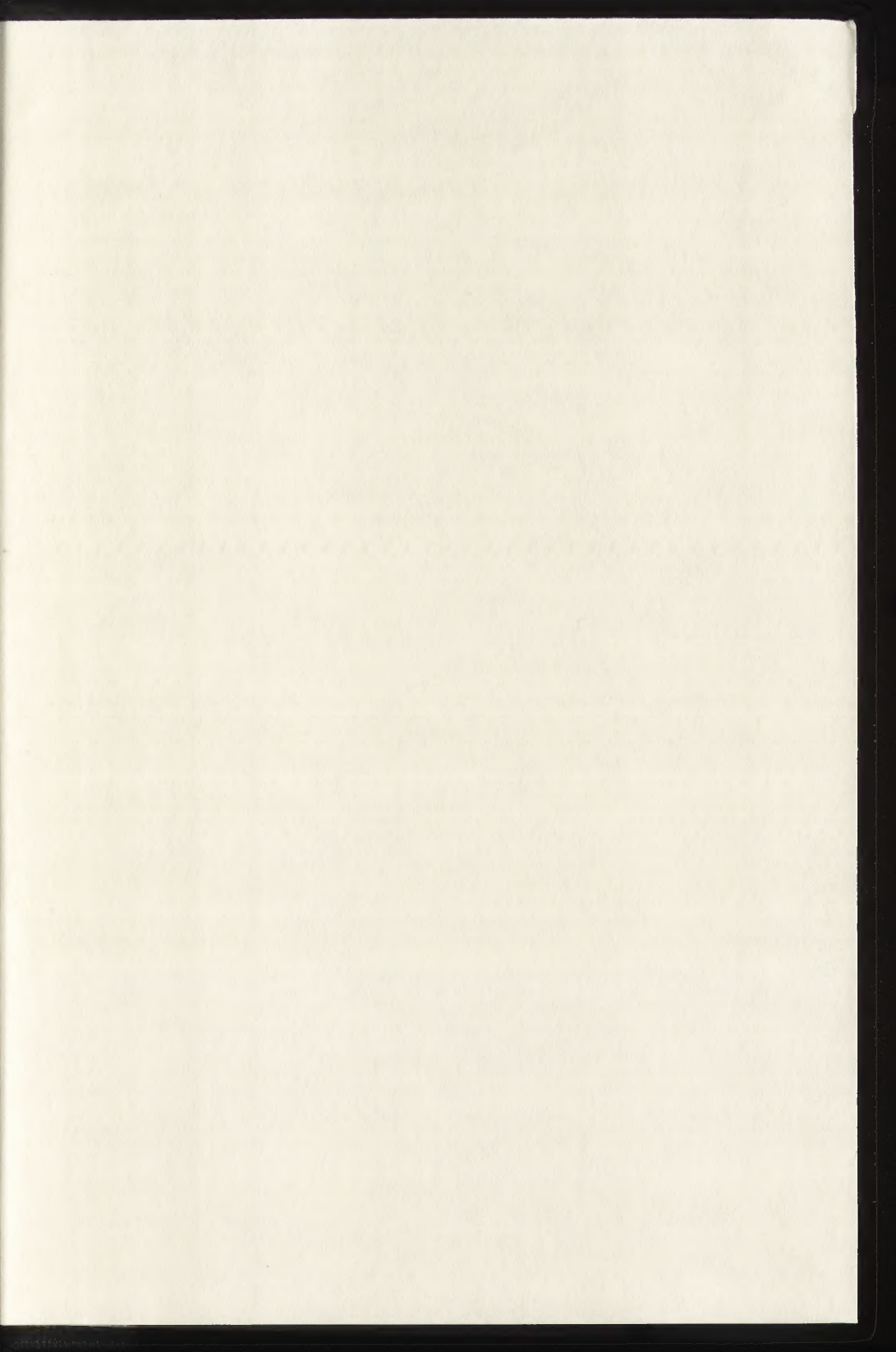
In conclusion I deem it proper to refer to the photogrammetric method, which appears to me extremely useful to the different stages I pointed out before. Photogrammetrical relief is in fact particularly apt to satisfy the different needs both in the filing and operative stages, as it rigorously and incontestably testifies the state of the works before they were laid hand upon. Finally photogrammetrical relief also provides a steady visual support for the readability of a work in its spacial and architectural relationship with its original place in case the work has been moved to a museum.

- (°) The author has taken part in the Symposium with his communication "Sulla necessità di formare restauratori di mosaici" (On the necessity of training mosaic restorers). (The Proceedings are being printed).
- (°°)cf. C. Robotti, Una sinopia musiva pavimentale a Stabia (A floor-mosaic sinopia at Stabiae), in "Bollettino d'Arte" del Min. Pubblica Istruzione, I, 1973, pp. 42-44.

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